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PYRAZOLE COMPOUNDS, PROCESS FOR PREPARING THE SAME, AND AGROHORTICULTURAL BACTERICIDES

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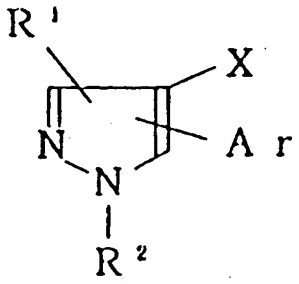
International Search Report

Abstract

Pyrazole compounds represented by general formula (I-1) or salts thereof, wherein R^1 represents a C_{1-6} haloalkyl or cyano group; R^2 represents a hydrogen atom, a metal atom, or the like; X represents a hydrogen atom, a halogen atom, a C_{1-6} alkyl group, or the like; Ar represents a 2-pyridyl, 2-pyrazyl, 2-pyrimidyl, or 2-thiazolyl group, these groups being optionally substituted with a halogen atom, a C_{1-6} alkyl, C_{1-6} alkenyl, C_{1-6} alkynyl, C_{3-5} cycloalkyl, C_{1-6} alkoxy, C_{1-6} haloalkyl group, or the like, excluding the case wherein R^1 represents CF_3, Ar represents 2-pyridyl, and X and R^2 both represent a hydrogen atom. Since the compounds have an excellent bactericidal activity



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MG	Madagascar
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ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
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VN	Vietnam
YU	Yugoslavia

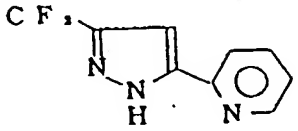
Technical field

The present invention relates to novel pyrazole compounds, processes for preparing the same, and agrohorticultural bactericides.

Prior art

Many agents for controlling plant diseases are used in the cultivation of agrohorticultural plants. However, for the following reasons, few of these controlling agents can be considered to be adequate in all cases. Drawbacks of these agents include an insufficient controlling effect, restrictions on use brought about by the appearance of agent-resistant disease-causing bacteria, the occurrence of pollution and chemical poisoning of plants, and toxicity of the agent to humans, livestock, and fish. As a result, there is a strong demand for an agent that can be used safely and does not have the shortcomings described above.

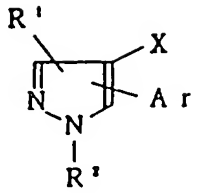
Technology that is relevant to the present invention is described in U.S. Patent No. 3,200,128, which discloses the compounds noted below as being useful as medicinal antibacterial agents. A description of the synthesis of this compound is included in the aforesaid publication, however, no specific description of test examples is provided, and nothing is written about the use of these compounds as agrohorticultural bactericides.



Disclosure of the invention

The object of the present invention is to present novel pyrazole compounds that can be used as agrohorticultural bactericides, and which can be safely produced, profitably and industrially synthesized, and have a reliable effect.

The present invention comprises the pyrazole compounds or salts thereof represented by general formula (I-1) (excluding cases in which R^1 represents CF_3, Ar represents 2-pyridyl, and X and R^2 are both hydrogen atoms).



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(Where R^1 represents a C_{1-6} haloalkyl group such as a difluoromethyl, trifluoromethyl, difluorochloromethyl, fluorochloromethyl, trichloromethyl, tribromomethyl, trifluoroethyl, or pentafluoroethyl group, etc.; a C_{1-6} alkoxycarbonyl group such as a methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, isopropoxycarbonyl, and butoxycarbonyl group, etc.; a carboxy group; a cyano group, a C_{1-6} alkylthio group such as a methylthio, ethylthio, propylthio, isopropylthio, butylthio, or t-butylthio group, etc.; a C_{1-6} alkylsulfinyl group such as a methylsulfinyl, ethylsulfinyl, propylsulfinyl, isopropylsulfinyl, butylsulfinyl, t-butylsulfinyl, pentylsulfinyl, or a hexylsulfinyl group, etc.; a C_{1-6} alkylsulfonyl group such as a methylsulfonyl, ethylsulfonyl group, propylsulfonyl, isopropylsulfonyl, butylsulfonyl, t-butylsulfonyl, pentylsulfonyl, or a hexylsulfonyl group, etc.; a hydroxy group; a C_{1-6} alkoxy group such as a methoxy, ethoxy, propoxy, isopropoxy, butoxy, or t-butoxy group, etc.; a thiocarbamoyl group; a hydroxyiminomethyl group; a C_{1-6} alkoxyiminomethyl group such as a methoxyiminomethyl, an ethoxyiminomethyl, or a propoxyiminomethyl group, etc.; a C_{1-6} alkoxymethyl group such as a dimethoxymethyl or a diethoxymethyl group, etc.; an amino group or a carbamoyl group, etc.;

R^2 represents a hydrogen atom; a heavy metal atom such as copper, lead, tin, manganese, nickel, cobalt or iron, etc.; a C_{1-6} alkoxy C_{1-6} alkyl group such as a methoxymethyl, ethoxymethyl, propoxymethyl, isopropoxymethyl, butoxymethyl, t-butoxymethyl, hexyloxymethyl, methoxyethyl, ethoxyethyl, propoxyethyl, isopropoxyethyl, butoxyethyl, t-butoxyethyl, hexyloxyethyl, methoxypropyl, ethoxypropyl, propoxypropyl, isopropoxypropyl, or a butoxypropyl, etc.; a C_{1-6} alkylcarbonyloxymethyl group such as an acetoxymethyl, propionyloxymethyl, propylcarbonyloxymethyl, isopropylcarbonyloxymethyl, butylcarbonyloxymethyl, t-butylcarbonyloxymethyl, pentylcarbonyloxymethyl, or a hexylcarbonyloxydimethyl group, etc.; a C_{1-6} alkylthiomethyl group such as a methylthiomethyl, ethylthiomethyl, propylthiomethyl, isopropylthiomethyl, butylthiomethyl, t-butylthiomethyl, hexylthiomethyl group, etc.; a C_{1-6} alkylsulfinylmethyl group such as a methylsulfinylmethyl, ethylsulfinylmethyl, propylsulfinylmethyl, isopropylsulfinylmethyl, butylsulfinylmethyl, t-butylsulfinylmethyl, or a hexylsulfinylmethyl group, etc.; a C_{1-6} alkylsulfonylmethyl group

such as a methylsulfonylmethyl, an ethylsulfonylmethyl, propylsulfonylmethyl, isopropylsulfonylmethyl, butylsulfonylmethyl, t-butylsulfonylmethyl, or a hexylsulfonylmethyl group, etc.; a benzoyl group optionally substituted with a (halogen atom, C_{1-4} alkyl group, C_{1-4} alkoxy group, a C_{1-4} haloalkyl group, a C_{1-4} haloalkoxy group, or a nitro group), etc.; a C_{1-6} alkylcarbonyl group such as an acetyl, propionyl, propylcarbonyl, isopropylcarbonyl, butylcarbonyl, t-butylcarbonyl, or a hexylcarbonyl group, etc.; a C_{1-6} alkoxycarbonyl group such as a methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, or an isopropoxycarbonyl group, etc.; a C_{1-6} alkylsulfonyl group such as a methylsulfonyl, ethylsulfonyl, propylsulfonyl group, isopropylsulfonyl, butylsulfonyl, t-butylsulfonyl, or pentylsulfonyl group etc.; a benzoyloxymethyl group optionally substituted with a (halogen atom, C_{1-4} alkyl group, C_{1-4} alkoxy group, a C_{1-4} haloalkyl group, a C_{1-4} haloalkoxy group, or a nitro group), etc.; a C_{1-6} alkoxycarbonyloxymethyl group such as a methoxycarbonyloxymethyl, ethoxycarbonyloxymethyl, propoxycarbonyloxymethyl, isopropoxycarbonyloxymethyl, butoxypropoxycarbonyloxymethyl, butoxycarbonyloxymethyl, or a t-butoxycarbonyloxymethyl group, etc.; a phenylsulfonyl group optionally substituted with a (halogen atom, C_{1-4} alkyl group, C_{1-4} alkoxy group, a C_{1-4} haloalkyl group, a C_{1-4} haloalkoxy group, or a nitro group), etc.; an N-C_{1-6} alkyl-N-C_{1-6} alkylcarbonylaminomethyl group such as an N-methyl-N-acetylaminomethyl, N-ethyl-N-acetylaminomethyl, N-propyl-N-acetylaminomethyl, N-isopropyl-N-acetylaminomethyl, N-butyl-N-acetylaminomethyl, N-t-butyl-aretylaminomethyl, or an
N-methyl-N-propionylaminomethyl group, etc.; an N,N-di C_{1-6} alkylthiocarbamoylthiomethyl group such as an N,N-dimethylthiocarbamoylthiomethyl, N,N-diethylthiocarbamoylthiomethyl, or an N-methyl-N-ethylthiocarbamoylthiomethyl group, etc.;

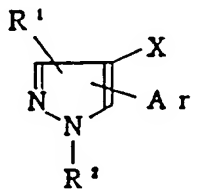
X represents a hydrogen atom; a halogen atom such as a fluorine atom, a chlorine atom; a formyl group; or a C_{1-6} alkyl group such as a methyl, ethyl, propyl, isopropyl, butyl, or t-butyl group;

Ar represents a 2-pyridyl group optionally substituted with a hydrogen atom; a halogen atom (such as a fluorine atom, a chlorine atom, etc.);a C_{1-6} alkyl group such as a methyl, ethyl, propyl, isopropyl, etc.; a C_{1-6} haloalkyl group such as a fluoromethyl, 1-fluoroethyl, 2-fluoroethyl, trifluoromethyl, chloromethyl, dichloromethyl, or trichloromethyl group, etc.; a C_{1-6} alkoxy C_{1-6} alkyl group such as a methoxymethyl, ethoxymethyl, propoxymethyl, methoxyethyl, ethoxyethyl, propoxypropyl, isopropoxymethyl or a isopropoxyethyl group, etc.; a hydroxymethyl group; C_{1-6} hydroxyalkyl group such as a 1-hydroxyethyl, 2-hydroxyethyl, 1-hydroxypropyl, 2-hydroxypropyl, or a 3-hydroxypropyl group, etc.; a C_{1-6} alkylsulfonyl C_{1-6} alkyl group such as a methylsulfonylmethyl, ethylsulfonylmethyl, propylsulfonylmethyl, methylsulfonylethyl, ethylsulfonylethyl, or a propylsulfonylethyl group, etc.; a C_{1-6} cyanoalkyl

group such as a cyanomethyl, 1-cyanoethyl, 2-cyanoethyl, 1-cyanopropyl, 2-cyanopropyl, 3-cyanopropyl, 1-cyanobutyl, 2-cyanobutyl, or a 3-cyanobutyl group, etc.; a C_{1-6} hydroxyiminoalkyl group such as a hydroxyiminomethyl, hydroxyiminoethyl, or a hydroxyiminopropyl group, etc.; a C_{1-6} alkoxyimino C_{1-6} alkyl group such as a methoxyiminomethyl, 1-methoxyiminoethyl, or 2-ethoxyiminoethyl group, etc.; a C_{1-6} alkylcarbonylhydrazino C_{1-6} alkyl group such as an acetylhydrazinomethyl, acetylhydrazinoethyl, propionylhydrazinomethyl, or propionylhydrazinoethyl group, etc.; a C_{1-4} alkoxy C_{1-4} alkoxy C_{1-6} alkyl group such as a methoxymethoxymethyl, ethoxymethoxymethyl, methoxyethoxymethyl, ethoxyethoxymethyl, methoxymethoxyethyl, ethoxymethoxyethyl, or ethoxyethoxyethyl group, etc.; a C_{2-6} alkenyl group such as vinyl, 1-propenyl, aryl, crotyl, or butadienyl group, etc.; a C_{2-6} haloalkenyl group such as a 1-chlorovinyl, 2-chlorovinyl, 3-chlorovinyl or 2-chlorocrotyl group, etc.; a C_{2-6} cyanoalk alkenyl group such as a 1-cyanovinyl or 2-cyanovinyl group, etc.; a C_{1-6} alkoxycarbonyl C_{2-6} alkenyl group such as a 1-methoxycarbonylvinyl, 2-methoxycarbonylvinyl, 1-methoxycarbonylallyl, 2-methoxycarbonylallyl, or a 3-methoxycarbonylallyl group, etc.; a C_{1-4} alkoxy C_{2-6} alkenyl group such as a 1-methoxyvinyl, 2-methoxyvinyl, 1-methoxyallyl, 2-methoxyallyl, or a 3-methoxyallyl group, etc.; a C_{2-6} alkynyl group such as an ethynyl, 1-propynyl, or a 2-propynyl group, etc.; a C_{2-6} haloalkynyl group such as a 2-chloroethynyl, 2-bromoethynyl, 3-chloro-2-propynyl, 3,3,3-trifluoro-1-propynyl group, etc.; a C_{2-6} hydroxyalkynyl group such as a 3-hydroxy-1-propynyl, or a 3-hydroxypropargyl group, etc.; a trimethylsilyl-substituted C_{2-6} alkynyl group such as a 2-trimethylsilylethynyl, or a 3-trimethylsilylpropargyl group, etc.; a C_{1-6} alkoxy C_{2-6} alkynyl group such as a 2-methoxyethynyl, 2-ethoxyethynyl, 2-propoxyethynyl, 3-methoxypropargyl, 3-ethoxypropargyl, or a 3-methoxy-1-propynyl group, etc.; a C_{1-3} dialkylamino group such as a methylamino, ethylamino, dimethylamino, or a diethylamino group, etc.; an amino group; a C_{1-6} alkylthio group such as a methylthio, ethylthio, propylthio, or isopropylthio group, etc.; a C_{1-6} haloalkylthio group such as chloromethylthio, fluoromethylthio, or a trifluoromethylthio group, etc., a C_{1-6} alkylsulfinyl group such as methylsulfinyl, or an ethylsulfinyl group, etc.; a C_{1-6} alkylsulfonyl group such as a methylsulfonyl or an ethylsulfonyl group, etc.; a C_{1-6} alkoxycarbonyl group such as a methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, or isopropoxycarbonyl group, etc.; a C_{3-6} cycloalkyl group such as a cyclopropyl, cyclopentyl, or cyclohexyl group, etc.; a C_{1-6} alkylcarbonyl group such as an acetyl or a propionyl group, etc.; a cyanate group; a thiocyanate group; a C_{1-6} alkoxy group such as a methoxy, ethoxy, propoxy, isopropoxy, butoxy, or t-butoxy group, etc.; a C_{1-6} haloalkoxy group such as a trifluoromethoxy, 1,1,2,2-tetrafluoroethoxy, trichloromethoxy, or a difluoromethoxy group, etc.; a benzyloxy group; a hydroxy group; a C_{1-6} alkylcarbonyloxy group such as a methylcarbonyloxy, ethylcarbonyloxy, propylcarbonyloxy, or isopropylcarbonyloxy group, etc.; a

C_{1-6} haloalkylsulfonyloxy group such as trifluoromethylsulfonyloxy, trichloromethylsulfonyloxy, or a pentafluoroethylsulfonyloxy group, etc.; a 1,2-epoxy C_{2-6} alkyl group such as a 1,2-epoxyethyl group, or a 1,2-epoxypropyl group, etc.; a C_{1-4} alkylcarbamoyloxy group such as a methylcarbamoyloxy, ethylcarbamoyloxy, or propylcarbamoyloxy group, etc.; a nitro group (halogens such as fluorine, chlorine, and bromine; C_{1-6} alkyl groups such as methyl and ethyl groups; C_{1-6} alkoxy groups such as methoxy groups; C_{1-6} alkyl groups such as trifluoromethyl; C_{1-6} haloalkoxy groups or nitro groups such as trifluoromethoxy); a 2-pyridyl group optionally substituted with a phenyl group (optionally substituted with a halogen atom such as fluorine, chlorine, or bromine, etc.; a C_{1-6} alkyl group such as a methyl group or an ethyl group, etc., a C_{1-6} alkoxy group such as a methoxy group, etc.; a C_{1-6} haloalkyl group such as a trifluoromethyl group; a C_{1-6} haloalkoxy group such as a trifluoromethoxy group, etc.; or a nitro group); a benzyl group (optionally substituted with a halogen atom such as fluorine, chlorine, or bromine, etc.; a C_{1-6} alkyl group such as a methyl group or an ethyl group, etc., a C_{1-6} alkoxy group such as a methoxy group, etc.; a C_{1-6} haloalkyl group such as a trifluoromethyl group; a C_{1-6} haloalkoxy group such as a trifluoromethoxy group, etc.; or a nitro group); a 2-pyrimidyl group (optionally substituted with a halogen atom such as fluorine, chlorine, or bromine, etc.; a C_{1-6} alkyl group such as a methyl group or an ethyl group, etc., a C_{1-6} alkoxy group such as a methoxy group, etc.; a C_{1-6} haloalkyl group such as a trifluoromethyl group); a 2-pyrazinyl group (optionally substituted with a halogen atom such as fluorine, chlorine, or bromine, etc.; a C_{1-6} alkyl group such as a methyl group or an ethyl group, etc., a C_{1-6} alkoxy group such as a methoxy group, etc.; a C_{1-6} haloalkyl group such as a trifluoromethyl group); or a 2-thiazolyl group (optionally substituted with a halogen atom such as fluorine, chlorine, or bromine, etc.; a C_{1-6} alkyl group such as a methyl group or an ethyl group, etc., a C_{1-6} alkoxy group such as a methoxy group, etc.; a C_{1-6} haloalkyl group such as a trifluoromethyl group.))

The present invention also comprises an agrohorticultural bactericide containing as an effective ingredient 1, 2 or more of the following pyrazole compounds or salts thereof represented by general formula (I-2).



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(Where R^1 represents a C_{1-6} haloalkyl group such as a difluoromethyl, trifluoromethyl, difluorochloromethyl, fluorochloromethyl, trichloromethyl, tribromomethyl, trifluoroethyl, or

pentafluoroethyl group, etc.; a C_{1-6} alkoxycarbonyl group such as a methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, isopropoxycarbonyl, and butoxycarbonyl group, etc.; a carboxy group; a cyano group, a C_{1-6} alkylthio group such as a methylthio, ethylthio, propylthio, isopropylthio, butylthio, or t-butylthio group, etc.; a C_{1-6} alkylsulfonyl group such as a methylsulfinyl, ethylsulfinyl, propylsulfinyl, isopropylsulfinyl, butylsulfinyl, t-butylsulfinyl, pentylsulfinyl, or hexylsulfinyl group, etc.; a C_{1-6} alkylsulfonyl group such as a methylsulfonyl, ethylsulfonyl group, propylsulfonyl, isopropylsulfonyl, butylsulfonyl, t-butylsulfonyl, pentylsulfonyl, or a hexylsulfonyl group, etc.; a hydroxy group; a C_{1-6} alkoxy group such as a methoxy, ethoxy, propoxy, isopropoxy, butoxy, or t-butoxy group, etc.; a thiocarbamoyl group; a hydroxyiminomethyl group; a C_{1-6} alkoxyiminomethyl group such as a methoxyiminomethyl, an ethoxyiminomethyl, or a propoxyiminomethyl group, etc.; a C_{1-6} alkoxymethyl group such as a dimethoxymethyl or a diethoxymethyl group, etc.; an amino group or a carbamoyl group, etc.

R^2 represents a hydrogen atom; a heavy metal atom such as copper, lead, tin, manganese, nickel, cobalt or iron, etc.; a C_{1-6} alkoxy C_{1-6} alkyl group such as a methoxymethyl, ethoxymethyl, propoxymethyl, isopropoxymethyl, butoxymethyl, t-butoxymethyl, hexyloxymethyl, methoxyethyl, ethoxyethyl, propoxyethyl, isoproxyethyl, butoxyethyl, t-butoxyethyl, hexyloxyethyl, methoxypropyl, ethoxypropyl, propoxypropyl, isopropoxypropyl, or butoxypropyl, etc.; a C_{1-6} alkylcarbonyloxymethyl group such as an acetoxymethyl, propionyloxymethyl, propylcarbonyloxymethyl, isopropylcarbonyloxymethyl, butylcarbonyloxymethyl, t-butylcarbonyloxymethyl, pentylcarbonyloxymethyl, or a hexylcarbonyloxydimethyl group, etc.; a C_{1-6} alkylthiomethyl group such as a methylthiomethyl, ethylthiomethyl, propylthiomethyl, isopropylthiomethyl, butylthiomethyl, t-butylthiomethyl, hexylthiomethyl group, etc.; a C_{1-6} alkylsulfinylmethyl group such as a methylsulfinylmethyl, ethylsulfinylmethyl, propylsulfinylmethyl, isopropylsulfinylmethyl, butylsulfinylmethyl, t-butylsulfinylmethyl, or a hexylsulfinylmethyl group, etc.; a C_{1-6} alkylsulfonylmethyl group such as a methylsulfonylmethyl, an ethylsulfonylmethyl, propylsulfonylmethyl, isopropylsulfonylmethyl, butylsulfonylmethyl, t-butylsulfonylmethyl, or a hexylsulfonylmethyl group, etc.; a benzoyl group optionally substituted with a (halogen atom, C_{1-4} alkyl group, C_{1-4} alkoxy group, a C_{1-4} haloalkyl group, a C_{1-4} haloalkoxy group, or a nitro group), etc.; a C_{1-6} alkylcarbonyl group such as an acetyl, propionyl, propylcarbonyl, isopropylcarbonyl, butylcarbonyl, t-butylcarbonyl, or a hexylcarbonyl group, etc.; a C_{1-6} alkoxycarbonyl group such as a methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, or an isopropoxycarbonyl group, etc.; a C_{1-6} alkylsulfonyl group such as a methylsulfonyl, ethylsulfonyl, propylsulfonyl group, isopropylsulfonyl, butylsulfonyl, t-butylsulfonyl, or pentylsulfonyl group etc.; a benzoyloxymethyl group optionally substituted with a (halogen atom,

C_{1-4} alkyl group, C_{1-4} alkoxy group, a C_{1-4} haloalkyl group, a C_{1-4} haloalkoxy group, or a nitro group), etc.;
a C_{1-6} alkoxycarbonyloxymethyl group such as a methoxycarbonyloxymethyl, ethoxycarbonyloxymethyl, propoxycarbonyloxymethyl, isopropoxycarbonyloxymethyl, butoxypropoxycarbonyloxymethyl, butoxycarbonyloxymethyl, or a t-butoxycarbonyloxymethyl group, etc.; a phenylsulfonyl group optionally substituted with a (halogen atom, C_{1-4} alkyl group, C_{1-4} alkoxy group, a C_{1-4} haloalkyl group, a C_{1-4} haloalkoxy group, or a nitro group), etc.; an N-C_{1-6} alkyl-N-C_{1-6} alkylcarbonylaminomethyl group such as an N-methyl-N-acetylaminomethyl, N-ethyl-N-acetylaminomethyl, N-propyl-N-acetylaminomethyl, N-isopropyl-N-acetylaminomethyl, N-butyl-N-acetylaminomethyl, N-t-butyl-N-aretylaminomethyl, or an N-methyl-N-propionylaminomethyl group, etc.; an N,N-di C_{1-6} alkylthiocarbamoylthiomethyl group such as an N,N-dimethylthiocarbamoylthiomethyl, N,N-diethylthiocarbamoylthiomethyl, or an N-methyl-N-ethylthiocarbamoylthiomethyl group, etc.

X represents a hydrogen atom; a halogen atom such as a fluorine atom, a chlorine atom; a formyl group; or a C_{1-6} alkyl group such as a methyl, ethyl, propyl, isopropyl, butyl, or t-butyl group.

Ar represents a 2-pyridyl group optionally substituted with a hydrogen atom; a halogen atom (such as a fluorine atom, a chlorine atom, etc.);a C_{1-6} alkyl group such as methyl, ethyl, propyl, isopropyl, etc.; a C_{1-6} haloalkyl group such as a fluoromethyl, 1-fluoroethyl, 2-fluoroethyl, trifluoromethyl, chloromethyl, dichloromethyl, or trichloromethyl group, etc.; a C_{1-6} alkoxy C_{1-6} alkyl group such as a methoxymethyl, ethoxymethyl, propoxymethyl, methoxyethyl, ethoxyethyl, propoxypropyl, isopropoxymethyl or an isopropoxyethyl group, etc.; a hydroxymethyl group; C_{1-6} hydroxyalkyl group such as a 1-hydroxyethyl, 2-hydroxyethyl, 1-hydroxypropyl, 2-hydroxypropyl, or a 3-hydroxypropyl group, etc.; a C_{1-6} alkylsulfonyl C_{1-6} alkyl group such as a methylsulfonylmethyl, ethylsulfonylmethyl, propylsulfonylmethyl, methylsulfonylethyl, ethylsulfonylethyl, or a propylsulfonylethyl group, etc.; a C_{1-6} cyanoalkyl group such as a cyanomethyl, 1-cyanoethyl, 2-cyanoethyl, 1-cyanopropyl, 2-cyanopropyl, 3-cyanopropyl, 1-cyanobutyl, 2-cyanobutyl, or a 3-cyanobutyl group, etc.; a C_{1-6} hydroxyiminoalkyl group such as a hydroxyiminomethyl, hydroxyiminoethyl, or a hydroxyiminopropyl group, etc.; a C_{1-6} alkoxyimino C_{1-6} alkyl group such as a methoxyiminomethyl, 1-methoxyiminoethyl, or 2-ethoxyiminoethyl group, etc.; a C_{1-6} alkylcarbonylhydrazino C_{1-6} alkyl group such as an acetylhydrazinomethyl, acetylhydrazinoethyl, propionylhydrazinomethyl, or propionylhydrazinoethyl group, etc.; a C_{1-4} alkoxy C_{1-4} alkoxy C_{1-6} alkyl group such as a methoxymethoxymethyl, ethoxymethoxymethyl, methoxyethoxymethyl, ethoxyethoxymethyl, methoxymethoxyethyl, ethoxymethoxyethyl, or

ethoxyethoxyethyl group, etc.; a C_{2-6} alkenyl group such as vinyl, 1-propenyl, aryl, crotyl, or butadienyl group, etc.; a C_{2-6} haloalkenyl group such as a 1-chlorovinyl, 2-chlorovinyl, 3-chlorovinyl or 2-chlorocrotyl group, etc.; a C_{1-6} cyanoalkenyl group such as a 1-cyanovinyl or 2-cyanovinyl group, etc.; a C_{1-6} alkoxycarbonyl C_{2-6} alkenyl group such as a 1-methoxycarbonylvinyl, 2-methoxycarbonylvinyl, 1-methoxycarbonylallyl, 2-methoxycarbonylallyl, or a 3-methoxycarbonylallyl group, etc.; a C_{1-4} alkoxy C_{2-6} alkenyl group such as a 1-methoxyvinyl, 2-methoxyvinyl, 1-methoxyallyl, 2-methoxyallyl, or a 3-methoxyallyl group, etc.; a C_{2-6} alkynyl group such as an ethynyl, 1-propynyl, or a 2-propynyl group, etc.; a C_{2-6} haloalkynyl group such as a 2-chloroethynyl, 2-bromoethynyl, 3-chloro-2-propynyl, 3,3,3-trifluoro-1-propynyl group, etc.; a C_{2-6} hydroxyalkynyl group such as a 3-hydroxy-1-propynyl, or a 3-hydroxypropargyl group, etc.; a trimethylsilyl-substituted C_{2-6} alkynyl group such as a 2-trimethylsilylethynyl, or a 3-trimethylsilylpropargyl group, etc.; a C_{1-6} alkoxy C_{2-6} alkynyl group such as a 2-methoxyethynyl, 2-ethoxyethynyl, 2-propoxyethynyl, 3-methoxypropargyl, 3-ethoxypropargyl, or a 3-methoxy-1-propynyl group, etc.; a C_{1-3} dialkylamino group such as a methylamino, ethylamino, dimethylamino, or a diethylamino group, etc.; an amino group; a C_{1-6} alkylthio group such as a methylthio, ethylthio, propylthio, or isopropylthio group, etc.; a C_{1-6} haloalkylthio group such as chloromethylthio, fluoromethylthio, or a trifluoromethylthio group, etc.; a C_{1-6} alkylsulfinyl group such as methylsulfinyl, or an ethylsulfinyl group, etc.; a C_{1-6} alkylsulfonyl group such as a methylsulfonyl or an ethylsulfonyl group, etc.; a C_{1-6} alkoxycarbonyl group such as a methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, or isopropoxycarbonyl group, etc.; a C_{3-6} cycloalkyl group such as a cyclopropyl, cyclopentyl, or cyclohexyl group, etc.; a C_{1-6} alkylcarbonyl group such as an acetyl or a propionyl group, etc.; a cyanate group; a thiocyanate group; a C_{1-6} alkoxy group such as a methoxy, ethoxy, propoxy, isopropoxy, butoxy, or t-butoxy group, etc.; a C_{1-6} haloalkoxy group such as a trifluoromethoxy, 1,1,2,2-tetrafluoroethoxy, trichloromethoxy, or a difluoromethoxy group, etc.; a benzyloxy group; a hydroxy group; a C_{1-6} alkylcarbonyloxy group such as a methylcarbonyloxy, ethylcarbonyloxy, propylcarbonyloxy, or isopropylcarbonyloxy group, etc.; a C_{1-6} haloalkylsulfonyloxy group such as trifluoromethylsulfonyloxy, trichloromethylsulfonyloxy, or a pentafluoroethylsulfonyloxy group, etc.; a 1,2-epoxy C_{2-6} alkyl group such as a 1,2-epoxyethyl group, or a 1,2-epoxypropyl group, etc.; a C_{1-4} alkylcarbamoyloxy group such as a methylcarbamoyloxy, ethylcarbamoyloxy, or propylcarbamoyloxy group, etc.; a nitro group (halogens such as fluorine, chlorine, and bromine; C_{1-6} alkyl groups such as methyl and ethyl groups; C_{1-6} alkoxy groups such as methoxy groups; C_{1-6} alkyl groups such as trifluoromethyl; C_{1-6} haloalkoxy groups or nitro groups such as trilfuoromethoxy); a 2-pyridyl group optionally substituted with a phenyl group (optionally substituted with a halogen atom such as fluorine, chlorine, or bromine, etc.; a C_{1-6} alkyl group

such as a methyl group or an ethyl group, etc., a C_{1-6} alkoxy group such as a methoxy group, etc.; a C_{1-6} haloalkyl group such as a trifluoromethyl group; a C_{1-6} haloalkoxy group such as a trifluoromethoxy group, etc.; or a nitro group); a benzyl group (optionally substituted with a halogen atom such as fluorine, chlorine, or bromine, etc.; a C_{1-6} alkyl group such as a methyl group or an ethyl group, etc., a C_{1-6} alkoxy group such as a methoxy group, etc.; a C_{1-6} haloalkyl group such as a trifluoromethyl group; a C_{1-6} haloalkoxy group such as a trifluoromethoxy group, etc.; or a nitro group); a 2-pyrimidyl group (optionally substituted with a halogen atom such as fluorine, chlorine, or bromine, etc.; a C_{1-6} alkyl group such as a methyl group or an ethyl group, etc., a C_{1-6} alkoxy group such as a methoxy group, etc.; a C_{1-6} haloalkyl group such as a trifluoromethyl group); a 2-pyrazinyl group (optionally substituted with a halogen atom such as fluorine, chlorine, or bromine, etc.; a C_{1-6} alkyl group such as a methyl group or an ethyl group, etc., a C_{1-6} alkoxy group such as a methoxy group, etc.; a C_{1-6} haloalkyl group such as a trifluoromethyl group); or a 2-thiazolyl group (optionally substituted with a halogen atom such as fluorine, chlorine, or bromine, etc.; a C_{1-6} alkyl group such as a methyl group or an ethyl group, etc., a C_{1-6} alkoxy group such as a methoxy group, etc.; a C_{1-6} haloalkyl group such as a trifluoromethyl group.))

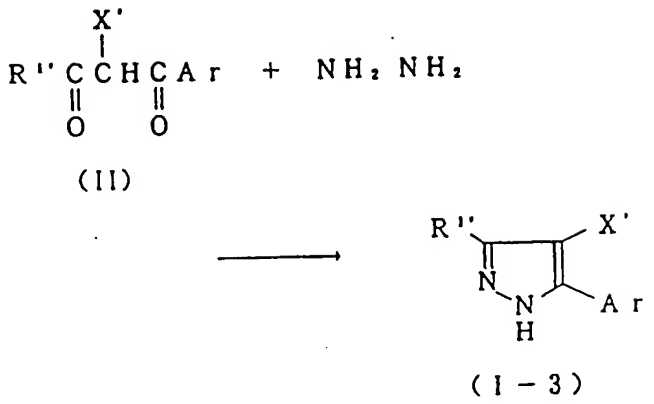
Moreover, the benzoyl, phenyl, pyridyl, pyrimidinyl, pyrazinyl and thiazolyl groups in the present invention may also contain 1, 2 or more substituents. In this case the substituents may be either the same or different.

Moreover, there are no particular restrictions regarding the salts of the pyrazole compounds of the present invention, provided they are salts that are agrohorticulturally acceptable. Examples of acceptable salts include salts of alkaline-earth metals such as magnesium, calcium, etc.; salts of heavy metals such as iron, copper, lead, nickel, cobalt, tin, manganese, etc.; salts of mineral acids such as hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, etc.; and salts of organic acids such as benzenesulfonic acid, oxalic acid, etc., optionally substituted with methanesulfonic acid, ethanesulfonic acid, or p-toluenesulfonic acid, etc.

Manufacture of compounds

The compounds of the present invention can be manufactured using the following processes.

Manufacturing method 1



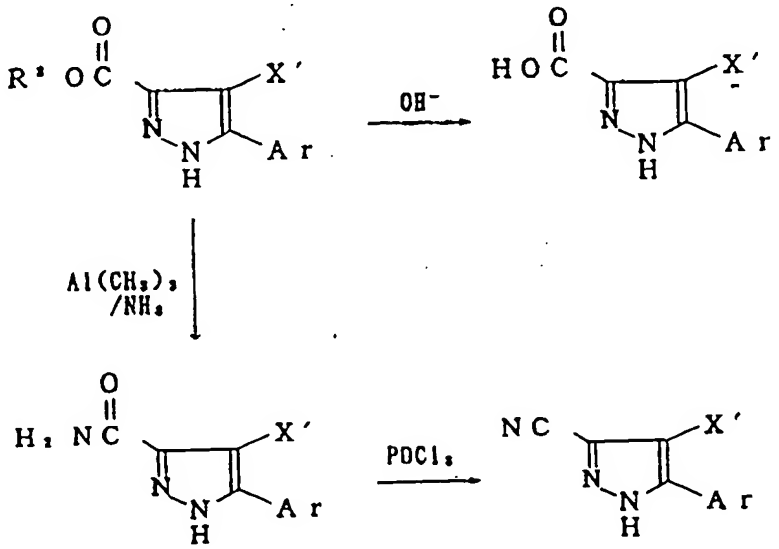
(II) (I－3)

(where $R^{1'}$ represents a C_{1-6} haloalkyl group, a C_{1-6} alkoxycarbonyl group, a C_{1-6} dialkoxymethyl group; X' represents a C_{1-6} alkyl group, and Ar has the same meaning described above)

This process is a method for manufacturing the compound expressed by formula (I-3) by reacting a compound expressed by general formula (II) with hydrazine without solvent or in an appropriate organic solvent between -50°C and 150°C.

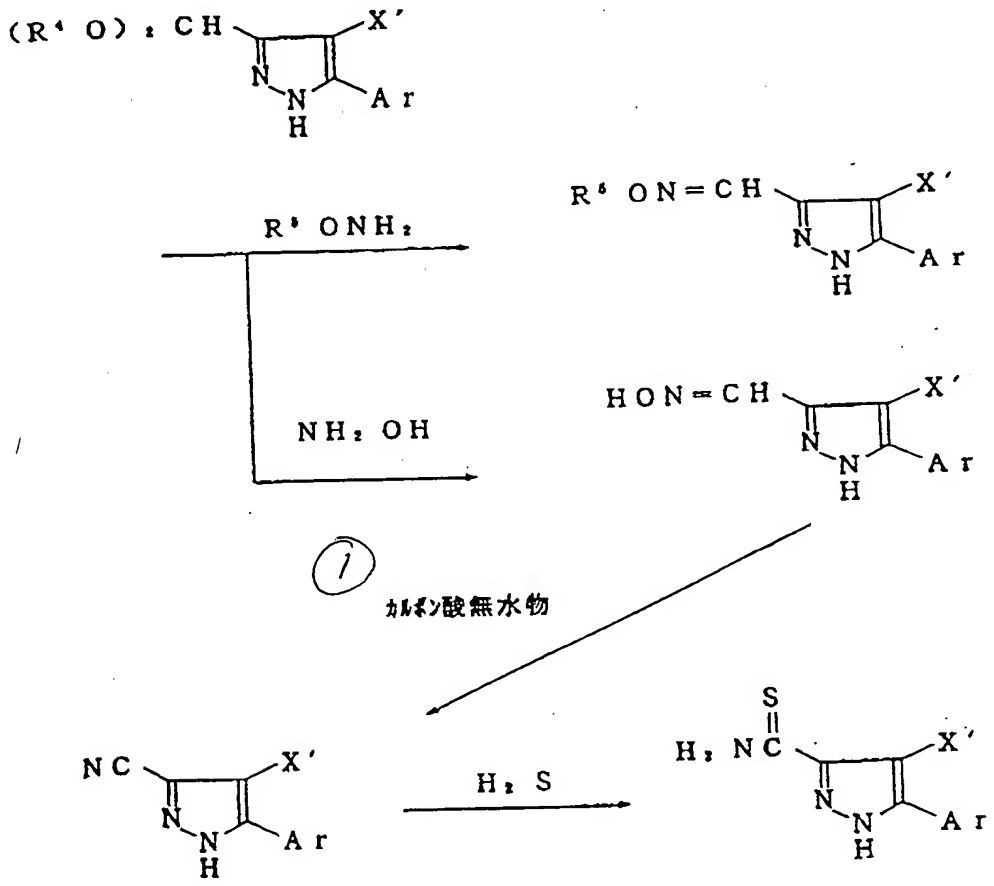
Examples of solvents that can be used in the reaction include water, alcohols such as methanol, ethanol, etc., and carboxylic acids such as acetic acid, etc. It is preferred if between 0.5-3 Eq of hydrazine per 1 Eq of compound (II) is used.

Among the compounds expressed by formula (I-3) obtained with the aforesaid manufacturing method, a compound in which $R^{1'}$ is a C_{1-6} alkoxycarbonyl group can be converted to a compound in which $R^{1'}$ is a carboxy group, a carbamoyl group, or a cyano group using ordinary processes of chemical synthesis. (See the schemes below.)



(Where R^3 represents a C_{1-6} alkyl group.)

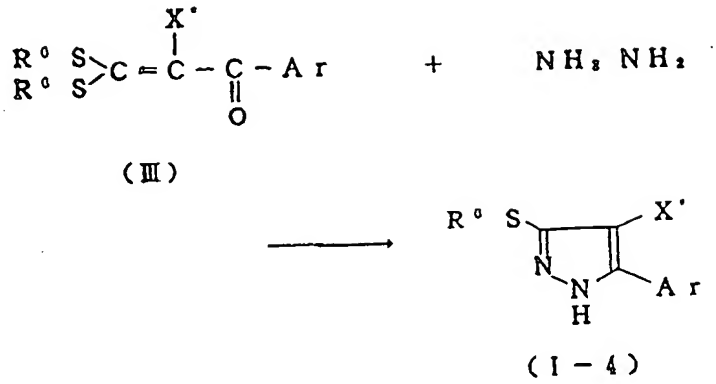
Among the compounds expressed by formula (I-3) obtained with the aforesaid manufacturing method, a compound in which $R^{1'}$ is a C_{1-6} alkoxymethyl group can be converted to a compound in which $R^{1'}$ is a hydroxyiminomethyl group, a C_{1-6} alkoxyiminomethyl group, a cyano group, or a thiocarbamoyl group using ordinary processes of chemical synthesis. (See the following scheme.)



Key: 1 Carboxylic acid anhydride

(Where R^4 and R^5 represent C_{1-6} alkyl groups.)

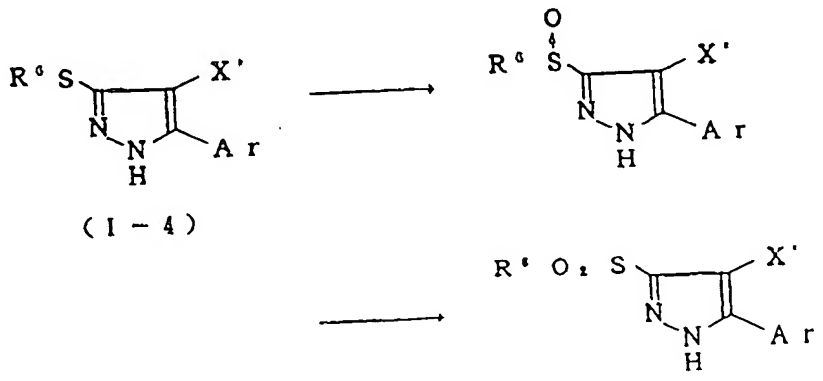
Manufacturing method 2



(where R^6 represents a C_{1-6} alkyl group, and X' and Ar have the same meanings described above.)

This process is a method for manufacturing the compound expressed by formula (I-4) by reacting the vinyl ketone expressed by general formula (III) with hydrazine without a solvent or in an appropriate organic solvent between -50°C and 150°C. Examples of solvents that can be used in the reaction include water, alcohols such as methanol, ethanol, etc., and carboxylic acids such as acetic acid, etc. It is preferred if between 0.5-3 Eq of hydrazine per 1 Eq of compound (III) is used.

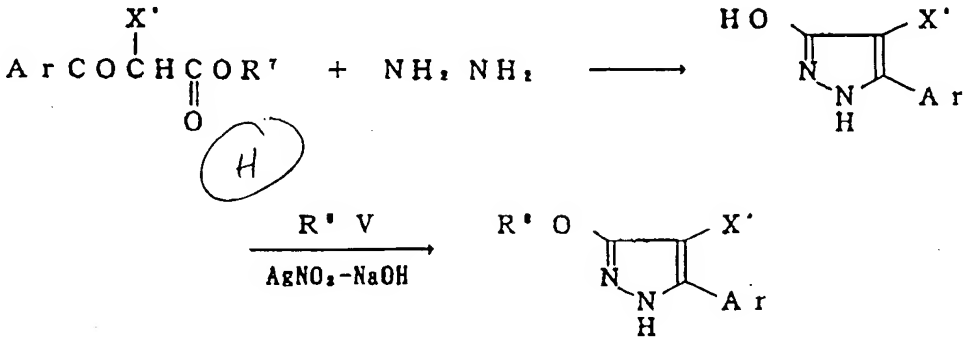
The compounds expressed by formula (I-4) obtained with the aforesaid manufacturing method can be converted to the corresponding alkylsulfinyl or alkylsulfonyl by conventional oxidation.



(Where R^6, X' and Ar have the same meanings described above.)

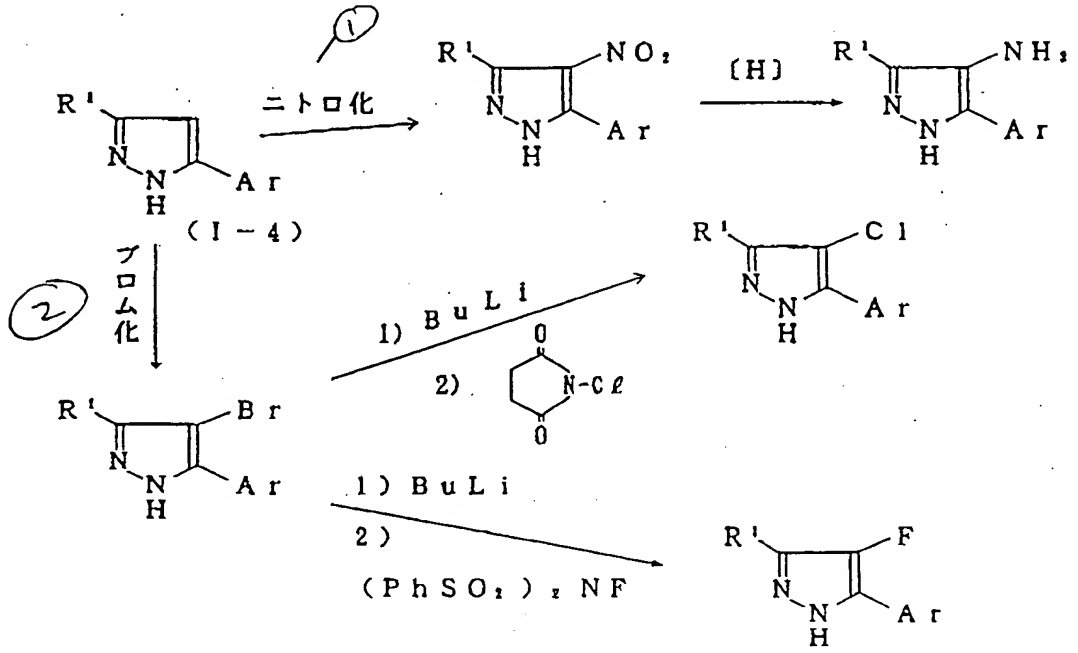
Manufacturing method 3

Compounds in which R^1 in formula (I-1) is a hydroxy group or a C_{1-6} alkoxy group can be manufactured using the following method.



(Where R^7 and R^8 represent C_{1-6} alkyl groups, and V represents a halogen atom.)

Manufacturing method 4

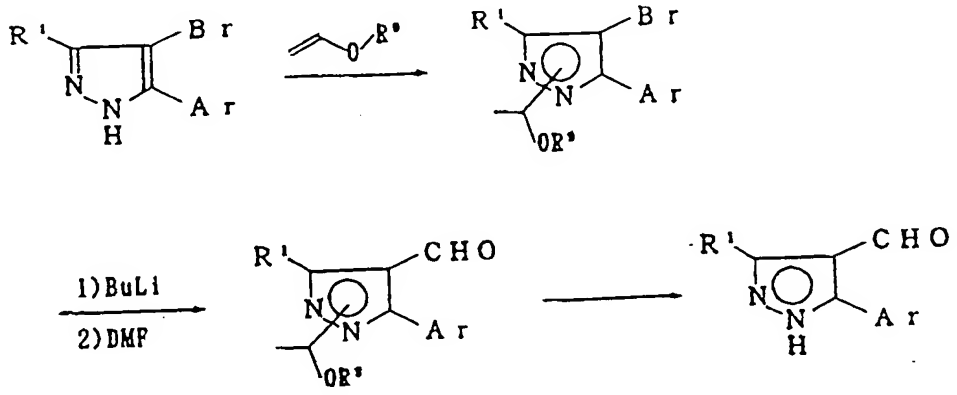


Key: 1 Nitration
2 Bromination

This method is used to manufacture compounds in which X in formula (I-1) is a nitro group or a halogen atom, by nitrating or halogenating the compounds expressed by formula (I-4) using conventional processes of chemical synthesis.

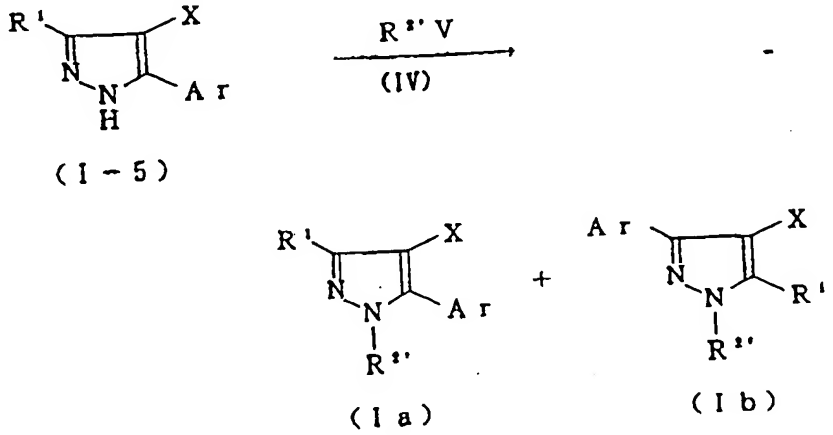
Moreover, by further reducing a compound in which X is a nitro group, compounds in which X is an amino group can also be manufactured.

With compounds in which X is a formyl group, by protecting the NH proton of the pyrazole ring with an appropriate protecting group, the corresponding bromo compound can be obtained using conventional techniques.



(Where R^9 represents a C_{1-6} alkyl group, and R^1 and Ar have the same meanings described above.)

Manufacturing method 5



This method is a process for manufacturing a compound in which R^2 in general formula (I-1) is something other than a hydrogen atom or a metal atom, by reacting a compound expressed by general formula (I-5) (where R^1, Ar, and X have the same meanings indicated above) and a reagent expressed by general formula (IV) (where $R^{2'}$ represents a group substituted from R^2, but not a hydrogen atom or a metal atom, V is a halogen atom), in the presence of a

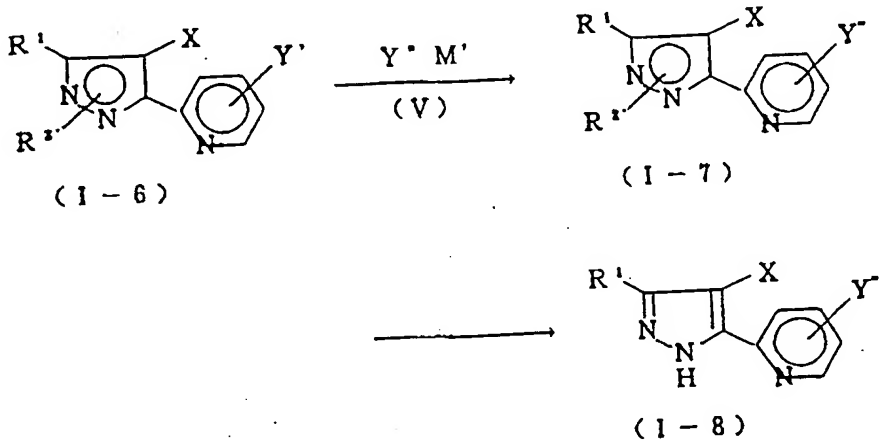
base between -50°C and 150°C. Usually, two products (Ia) and (Ib) in this reaction. Examples of the base used in this reaction include carbonates such as potassium carbonate or sodium carbonate, etc.; metal hydroxides such as sodium hydroxide, etc.; organic bases such as triethylamine, pyridine, etc.; and metal alkoxides such as sodium methylate, t-butoxy potassium, etc.

Examples of solvents that can be used in this reaction include aromatic hydrocarbons such as benzene and toluene, etc.; esters such as ethyl acetate, etc.; ethers such as diethyl ether, tetrahydrofuran (THF), etc.; halohydrocarbons such as chloroform, etc.; alcohols such as methanol and ethanol, etc.; acetonitrile, dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), etc. It is preferred if between 0.5-3 Eq of base and between 0.5-3 Eq of the compound in general formula (IV) are used per 1 Eq of the compound in general formula (I-5).

Manufacturing method 6

Among the compounds expressed by formula (I-1), compounds in which R^2 is a metal atom can be manufactured by dissolving 2 Eq of the compound expressed by formula (I-5) in an organic solvent such as acetone, or ethanol, etc., then adding to this an aqueous or ethanol solution of 1 Eq of a metal salt such as a metal chloride, etc.

Manufacturing method 7

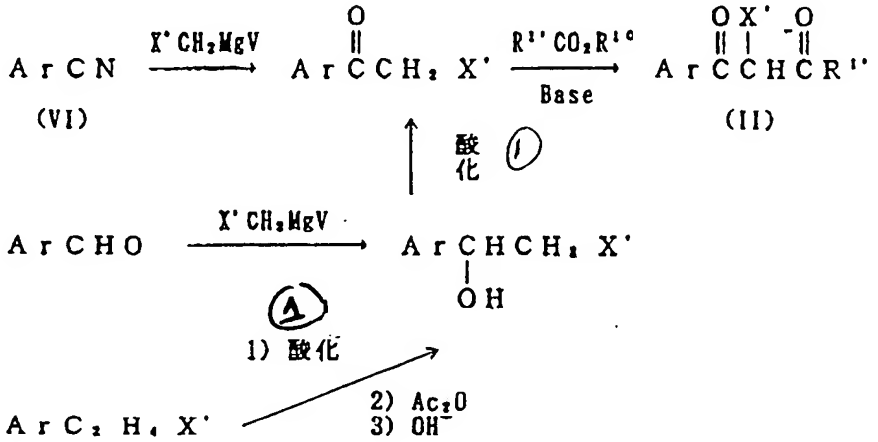


(Where R^1, X, and $R^{2'}$ have the same meanings noted above, and Y' represents a leaving group such as a trifluoromethanesulfonyloxy group or a halogen atom; and Y" represents a C_{1-6} alkyl group, C_{1-6} alkenyl group, C_{1-6} alkynyl group, C_{1-6} haloalkyl group, C_{1-6} haloalkenyl group, or a C_{1-6} haloalkynyl group, etc.)

This method is a process for manufacturing a compound expressed by formula (I-8). This is done by reacting a compound that has a leaving group such as a trifluoromethanesulfonyloxy

group or a halogen atom on the pyrazine ring of a compound expressed by formula (I-6), and a C_{1-6} alkyl, alkenyl, or alkynyl metal reagent (optionally substituted with a halogen atom) expressed by formula (V), in the presence of an suitable metal catalyst.

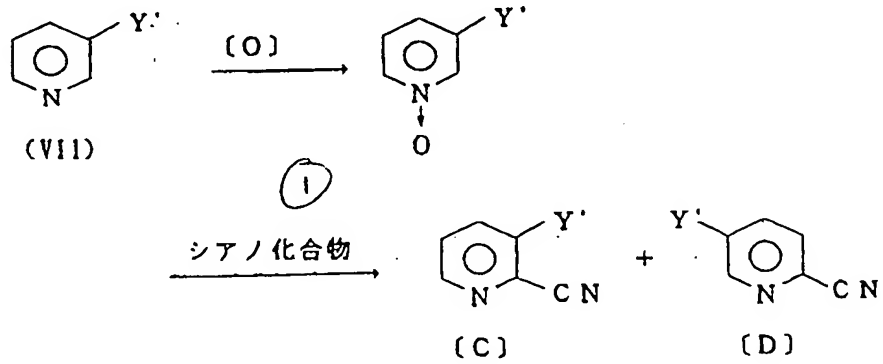
A compound (II) that is an intermediate material used in manufacturing method 1 can be obtained by any of the following methods.



Key: 1 Oxidation

(Where, R^{10} represents a C_{1-6} alkyl group, and V represents a halogen atom.)

Of the nitrile compounds expressed by formula (VI), a 2-cyanopyridine with a substituent in position 3 or 5 can be obtained by deriving a pyridine oxide from a pyridine compound with a substituent in the third position that are expressed by formula (VII), then reacting this with a cyanizing agent.



Key: 1 Cyano compound

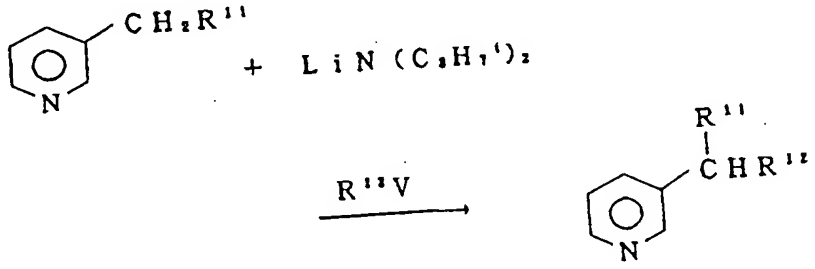
Examples of cyanizing agents for reacting with the pyridine oxide include combinations such as trimethylsilyl cyanide (TMSCN)-triethylamine, dimethylcarbamoyl chloride-sodium cyanate (NaCN), TMSCl-NaCN-triethamine, etc. Compound (C) or (D) can be obtained first by selecting these cyanizing agents appropriately.

Of the pyridine compounds with a substituent in the third position that are expressed by formula (VII), a compound in which Y' is an optionally substituted C_{1-6} alkyl group, an optionally substituted C_{2-6} alkenyl group or a C_{3-6} cycloalkyl group, can be obtained as shown below. For example, such a compound can be obtained by reacting a 3-bromopyridine with the corresponding Grignard reagent in the presence of a metal compound such as a nickel compound, etc.

Key: 1 Metal catalyst

(Where V represents a halogen atom, Y' represents an optionally substituted C_{1-6} alkyl group, an optionally substituted C_{2-6} alkenyl group or a C_{3-6} cycloalkyl group.)

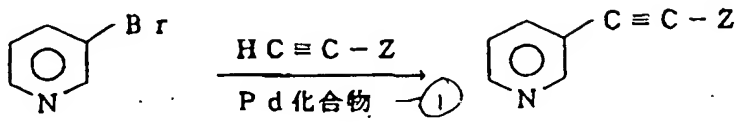
Of the pyridine compounds with a substituent in the third position that are expressed by formula (VII), a compound that has a branched alkyl, alkenyl, or alkynyl substituent in the α position can be obtained by the following method.



(Where R^{11} and R^{12} both represent a C_{1-6} alkyl or a C_{2-6} alkenyl or alkynyl group, and V represents a halogen atom).

Of the substituted pyridine compounds expressed by formula (VII), a compound that has a 1-alkynyl substituent can be obtained in the following way. For example, by reacting a

3-bromopyridine and an acetyl derivative corresponding thereto in the presence of a catalytic amount of a palladium compound.



Key: 1 Pd compound

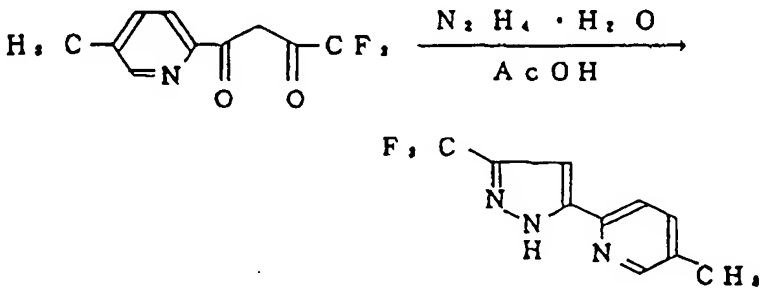
(Where Z represents a hydrogen atom, a halogen atom, a trimethylsilyl group, or a C_{1-6} alkoxy group, or a C_{1-4} alkyl group (optionally substituted with a hydroxy group or a C_{1-6} alkoxy group.)

Application examples

The present invention is further explained with application examples.

Application Example 1

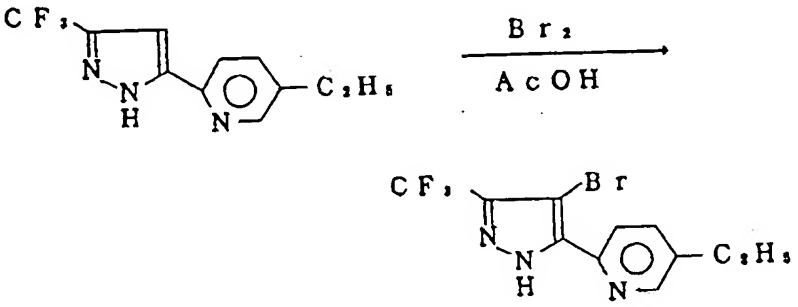
Manufacture of 5-(5-methyl-2-pyridyl)-3-trifluoromethyl pyrazole



Hydrazine hydrate (0.32 mL, 6.5 mmol) was added to an acetic solution (30 mL) of 4,4,4-trifluoro-1-(5-methyl-2-pyridyl)-butane-1,3-dione (1.00 g, 4.3 mmol), and was heated for 15 min at 90-95°C. After the reaction was completed, it was poured over ice water, the precipitate produced was filtered, and 0.59 g of the target compound was obtained at a yield of 60%. mp 150-151°C.

Application Example 2

Manufacture of 4-bromo-5-(5-ethyl-2-pyridyl)-3-trifluoromethylpyrazole

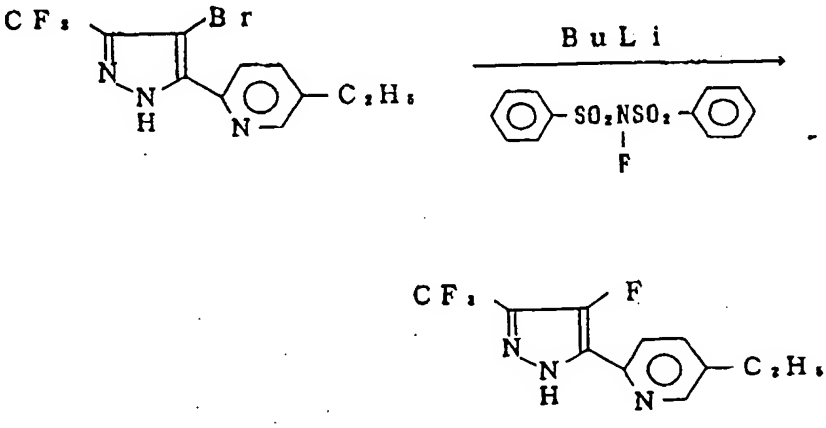


One gram of 5-(5-ethyl-2-pyridyl)-3-trifluoromethylpyrazole (4.1 mmol) was dissolved in 15 mL of acetic acid, then under stirring, 10 mL of an acetic acid solution of 0.8 g bromine (5 mmol) was added dropwise at room temperature. After stirring at room temperature overnight, the reaction liquid was poured into ice water and extracted with ethyl acetate. The ethyl acetate layer was washed first with an aqueous solution of sodium hydrogensulfite, then an aqueous solution of sodium hydrogencarbonate, then with water. It was then dried over anhydrous magnesium sulfate, and concentrated under reduced pressure.

The residue obtained was washed with n-hexane, and 1.15 g of the target compound were obtained. The yield was 87%, mp 181-182°C.

Application Example 3

Manufacture of 5-5(ethyl-2-pyridyl)-4-fluoro-3-trifluoromethyl pyrazole.



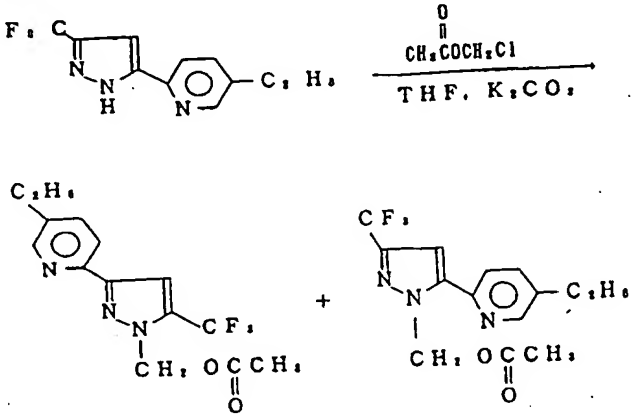
0.43 g of 4-bromo-5-(5-ethyl-2-pyridyl)-3-trifluoromethylpyrazole (1.34 mmol) was dissolved in 15 mL of dry tetrahydrofuran (THF), then 1.75 mL of an N-hexane solution of 1.69M n-butyllithium were added dropwise in a nitrogen gas flow under stirring at -78°C. After stirring the reaction liquid for one additional hour at the same temperature, 0.48 g of

N-fluorobenzenesulfonimide was added. The temperature of the reaction liquid was gradually increased to room temperature, then after stirring overnight, excess magnesium sulfuric acid anhydride was added. The reaction liquid was extracted with ethyl acetate, then rinsed with a saturated salt water, dried over anhydrous magnesium sulfate, and the solvent was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography, and 0.12 g of the target compound was obtained. The yield was 34%, mp 166-168°C.

By adding N-chlorosuccinimide instead of the N-fluorobenzenesulfonimide with the same reaction conditions described above, the corresponding 4-chloropyrazole can be obtained.

Application Example 4

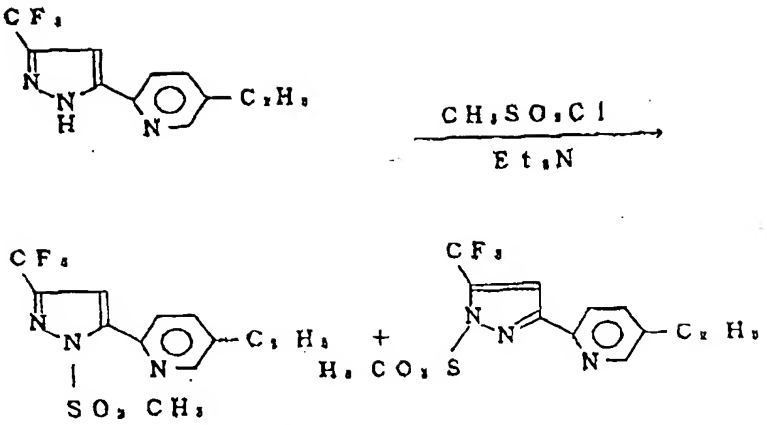
Manufacture of 1-acetoxymethyl-3-(5-ethyl-2-pyridyl)-5-trifluoromethylpyrazole and 1-acetoxymethyl-5-(5-ethyl-2-pyridyl)-3-trifluoromethylpyrazole



5-(5-ethyl-2-pyridyl)-3-trifluoromethylpyrazole (0.8 g) was dissolved in 20 mL of THF, and calcium carbonate (0.69 g) was added at room temperature. After stirring for 10 min at room temperature, chloromethylacetate (0.54 g) was added, and was heated and refluxed for 3 h. The reaction mixture was poured over ice water, extracted with ethyl acetate, and after washing the organic layer with saturated salt water, anhydrous magnesium sulfate was added for drying, and the solvent was distilled off under reduced pressure. The residue was purified with silica gel chromatography (solvent: benzene-ethyl acetate = 100:1), and 1-acetoxymethyl-3-(5-ethyl-2-pyridyl)-5-trifluoromethylpyrazole (0.57 g, yield of 55%, $n_D^{20.6}$ 1.5018), and 1-acetoxymethyl-5-(5-ethyl-2-pyridyl)-3-trifluoromethylpyrazole (0.12 g, yield of 12%, $n_D^{20.7}$ 1.5060).

Application Example 5

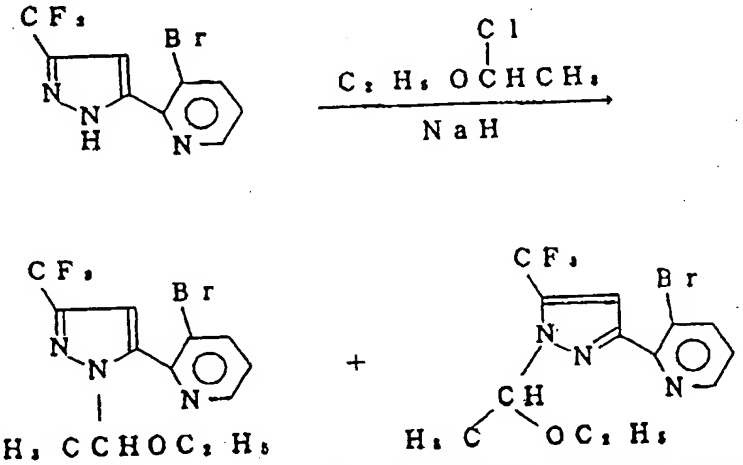
Manufacture of 3-(5-ethyl-2-pyridyl)-1-methylsulfonyl-5-trifluoromethylpyrazole and 5-(5-ethyl-2-pyridyl)-1-methylsulfonyl-3-trifluoromethylpyrazole



5-(5-ethyl-2-pyridyl)-3-trifluoromethylpyrazole (0.8 g) was dissolved in methylene chloride (20 mL), and triethylamine (0.37 g) was added at room temperature. After stirring for 5 min at room temperature, 0.5 g of methanesulfonyl chloride was added gradually, and a reaction was carried out for 2 h at room temperature. The reaction mixture was poured over ice water, and extracted with chloroform. The organic layer was rinsed with saturated salt water, anhydrous magnesium sulfate was added to dry it, and the solvent was distilled off under reduced pressure. The residue was purified by silica gel column chromatography (solvent benzene-ethyl acetate = 100:1), and 3-(5-ethyl-2-pyridyl)-1-methylsulfonyl-5-trifluoromethylpyrazole (0.54 g, yield 51%, mp 100-102°C) and 5-(5-ethyl-2-pyridyl)-1-methylsulfonyl-3-trifluoromethylpyrazole (0.31 g, 29% yield, NMR data shown in 1a-98 of Table 1-1).

Application Example 6

Manufacture of 1-(1-ethoxyethyl)-3-trifluoromethyl-5-(3-bromo-2-pyridyl)pyrazole and 1-(1-ethoxyethyl)-3-(3-bromo-2-pyridyl)-5-trifluoromethylpyrazole



4.2 g (1.106 mol) of 60% sodium hydride were added to 150 mL of dry DMF, then a solution of 25.7 g (0.088 mol) of 3-trifluoromethyl-5-(3-bromo-2-pyridyl)pyrazole dissolved in

150 mL of DMF was added dropwise to this under ice cooling. After stirring for 30 min at room temperature, it was ice-cooled again, then 12.4 g (0.114 mol) of 1-chloroethyl ethyl ether were added. After the dropwise addition, it was stirred for 1 h at room temperature, then allowed to react for 2 additional h between 50-60°C. The reaction liquid was concentrated under reduced pressure and the majority of the DMF was removed. Water and ether were added to the residue, and the liquids were separated. The organic layer was washed with water, then after drying and concentration, 31.3 g of an oily material that is to become the object of the process were obtained. At a yield of 98%, the ratio between the components was 5-CF_3 compound/3-CF_3 compound = 2/1.

^{1}H-NMR data of the mixture ($CDCl_3$, δ ppm):

(1) 5-CF_3 compound

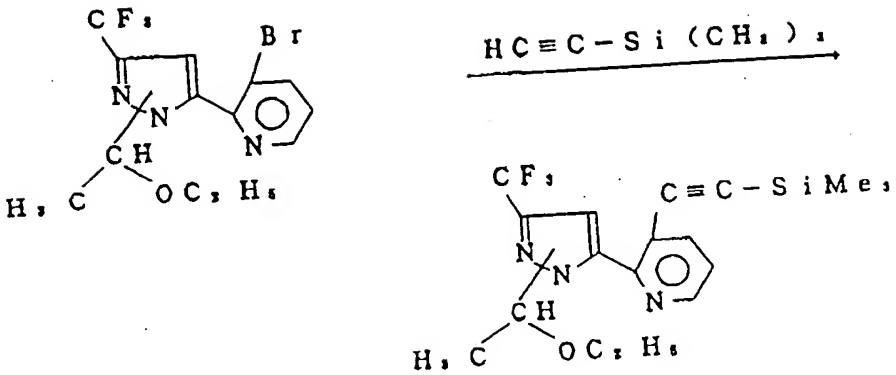
1.02 (3H, t)、1.78 (3H, d)、3.11－3.40 (2H, m)、5.60 (1H, q)、6.82 (1H, s)、7.28 (1H, dd)
8.07 (1H, d)、8.69 (1H, d)

(2) 3-CF_3 compound

1.19 (3H, t)、1.79 (3H, d)、3.40－3.57 (2H, m)、5.79 (1H, q)、7.17 (1H, dd)、7.28 (1H, s)
、8.02 (1H, d)、8.63 (1H, d)

Application Example 7

Manufacture of
1-(1-ethoxyethyl)-3-trifluoromethyl-5-[3-(2-trimethylsilylethynyl)-2-pyridyl]pyrazole and
1-(1-ethoxyethyl)-3-[3-(2-trimethylsilylethynyl)-2-pyridyl]-5-trifluoromethylpyrazole



10.0 g (27.4 mmol) of the mixture obtained in Application Example 6, 0.52 g (27 mmol) of cuprous iodide, and 0.96 g (1.4 mmol) bistriphenylphosphine dichloropalladium were added to 100 mL of triethylamine. Then under stirring, 3.5 g (35.6 mmol) of trimethylsilylacetylene were added to this, and it was heated and refluxed for 3 h. Next, an additional 3.5 g of trimethylsilylacetylene were added, and it was heated and refluxed again. The reaction liquid was then concentrated, water, chloroform, and Celite were added to the residue, and after filtration, the liquids were separated. By drying and concentrating the organic layer, a crude product of the target compound was obtained as an oily mixture. The yield was 13.0 g.

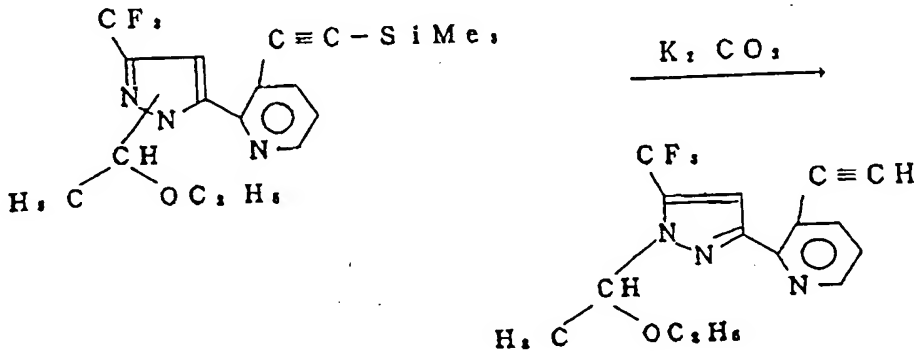
^{1}H-NMR data of the mixture ($CDCl_3$, δppm):

0.17 (9H. s)、1.02 (3H. t)、1.79 (3H. d)、3.13-3.31 (2H. m)、5.93 (1H. q)、7.00 (1H. s)、

7.31 (1H. dd)、7.90 (1H. d)、8.63 (1H. d)

Application Example 8

Manufacture of 1-(1-ethoxyethyl)-3-(3-ethynyl-2-pyridyl)-5-trifluoromethylpyrazole



13.0 g of the crude oily mixture obtained in Application Example 7 were dissolved in

130 mL of methanol, then 0.65 g of potassium carbonate was added, and it was stirred overnight at room temperature. The reaction liquid was concentrated under reduced pressure, water, chloroform and Celite were added, and after filtration, the liquids were separated. The residue obtained by washing the chloroform layer with water, drying and concentrating was purified by silica gel chromatography, and 4.40 g of the target material were obtained. The total yield beginning from Application Example 7 was 52%.

^{1}H-NMR data ($CDCl_3$, δppm):

(CDCl₃, δppm) : 1.02 (t, 3H), 1.80 (d, 3H), 3.14-3.30 (m, 2H), 3.34 (s, 1H), 5.93 (q, 1H), 6.99 (s, 1H), 7.36 (dd, 1H), 7.97 (d, 1H), 8.68 (d, 1H)

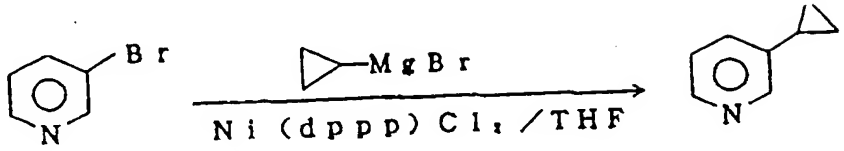
Application Example 9

Manufacture of 3-trifluoromethyl-5-(3-ethynyl-2-pyridyl)pyrazole

4.40 g of 1-(1-ethoxyethyl)-3-(3-ethynyl-2-pyridyl)-5-trifluoromethylpyrazole (0.0142 mol) were dissolved in 40 mL of methanol, then 5 mL of 1N hydrochloric acid were added dropwise under stirring. After dropwise addition of the acid, it was stirred for an additional 5 h at room temperature, then the reaction liquid was concentrated under reduced pressure. Then after washing the chloroform layer with water and drying it, it was concentrated under reduced pressure and white crystals were obtained. By recrystallization from benzene, 2.80 g of the target material were obtained. The yield was 84%, mp 140-141°C.

Reference Example 1

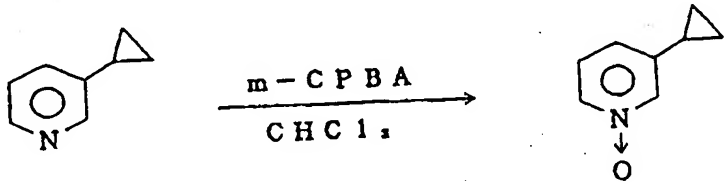
Manufacture of 3-cyclopropylpyridine



2.8 g (5.1 mmol) of Ni (dppp)Cl_2* were added to 8.0 g (50.6 mmol) of 3-bromopyridine and 100 mL of dry tetrahydrofuran (THF), and the air in the reaction vessel was replaced with nitrogen gas. This mixture was cooled to 0°C, then a tetrahydrofuran solution of a Grignard reagent compounded from 12.2 g (101.1 mmol) of cyclopropylbromide and 2.4 g (101.2 mmol) of magnesium was added dropwise to this mixture, then stirred for 2 h at room temperature. The reaction liquid was poured into aqueous ammonium chloride, then extracted with ethyl acetate. The ethyl acetate layer was washed with water, dried, then concentrated, and the residue obtained was purified by silica gel chromatography, and 4.2 g of the target material were obtained. The yield were 69%, bp 75°C/8 mmHg

Reference Example 2

Manufacture of 3-cyclopropylpyridine-N-oxide



4.2 g (35.3 mmol) of 3-cyclopropylpyridine were dissolved in 40 mL of chloroform, and cooled to 0°C. Then 8.4 g (38.8 mmol) of 80% pure m-chloroperbenzoic acid were added, and it was stirred overnight at room temperature. The precipitated m-chloroperbenzoic acid [sic] was filtered, the filtrate was washed with a saturated aqueous solution of sodium carbonate, dried and concentrated, and 4.6 g of the target substance was obtained. The yield was 96.4%.

^{1}H-NMR data of ($CDCl_3$, δppm):

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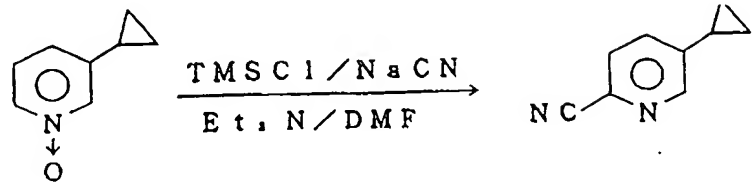
* Dichloro-1,3-bis(diphenylphosphine)propane nickel

(CDCl$_3$, δppm) : 0.73 (m, 2H), 1.06 (m, 1H), 1.80 (m, 1H), 6.94 (dd, 1H), 7.13 (t, 1H), 7.99 (dd, 1H)

Reference Example 3

Manufacture of 2-cyano-5-cyclopropylpyridine



4.4 g (32.6 mmol) of 3-cyclopropylpyridine-N-oxide were dissolved in 120 mL of N,N-dimethylformamide (DMF), and 13.2 g (130.4 mmol) of triethylamine and 4.8 g (97.8 mmol) of sodium cyanide were added, and after ice-cooling, 10.6 g (97.8 mmol) of trimethylsilylchloride were added dropwise. After dropwise addition, the reaction mixture was heated for 48 h at 100-110°C, the reaction liquid was concentrated under reduced pressure, water, chloroform, and Celite were added to the residue, and following filtration, the liquids were separated. The chloroform layer was rinsed with water, dried and concentrated, and the resulting residue was purified by silica gel column chromatography, whereby 2.0 g of the target substance were obtained. Yield was 43%.

^{1}H-NMR data (CDCl$_3$, δppm):

(CDCl$_3$, δppm) : 0.84 (m, 2H), 1.19 (m, 2H), 1.96 (m, 1H), 7.39 (dd, 1H), 7.58 (d, 1H), 8.49 (d, 1H)

Reference Example 4

Manufacture of 2-acetyl-5-cyclopropylpyridine

5.7 g (39.6 mmol) of 2-cyano-5-cyclopropylpyridine were dissolved in 50 mL of dried THF, and the air in the reaction vessel was replaced with nitrogen gas. The reaction liquid was

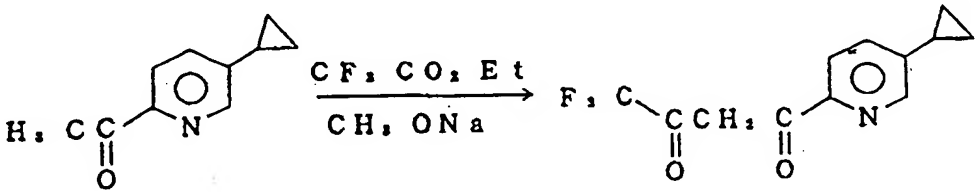
cooled to 0°C, then 16.0 mL (47.5 mmol) of a THF solution of 3.0M methylmagnesium chloride were added dropwise. After stirring for 2 h at room temperature, the reaction liquid was ice-cooled, and an aqueous solution of 1N-hydrochloric acid was added dropwise. Next, the mixture was made alkaline with an aqueous solution of 1N sodium hydroxide, and then extracted with chloroform. The chloroform layer was rinsed with water, dried and concentrated, and 6.1 g of the target material were obtained. The yield was 96%.

^{1}H-NMR data ($CDCl_3$, δppm):

0.80 (m, 2H), 1.12 (m, 2H), 1.95 (m, 1H), 2.68 (s, 3H), 7.36 (d, 1H), 7.91 (d, 1H), 8.42 (d, 1H)

Reference Example 5

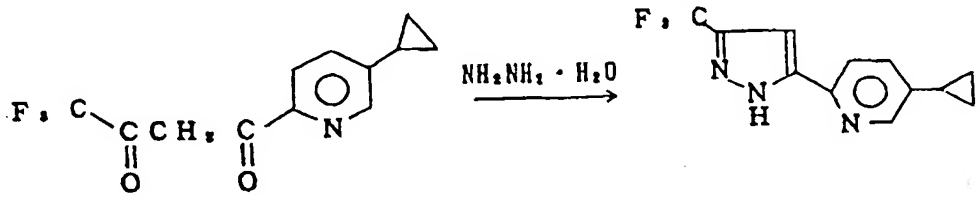
Manufacture of 4,4,4-trifluoro-1-(5-cyclopropyl-2-pyridyl)butane-1,3-dione



1.3 g (8.1 mmol) of 2-acetyl-5-cyclopropylpyridine and 1.9 g (13.7 mmol) of trifluoroethyl acetate were dissolved in 15 mL of THF, then 3.3 g (17.0 mmol) of a methanol solution of 28% sodium methoxide were added at room temperature. After stirring as is for 1 h, 1.1 g (18.3 mmol) of acetic acid were added to the reaction liquid. After concentration, the residue was dissolved in chloroform, rinsed with water, dried, and concentrated, and 1.9 g of the crude target material were obtained.

Application Example 10

Manufacture of 5-(5-cyclopropyl-2-pyridyl)-3-trifluoromethylpyrazole

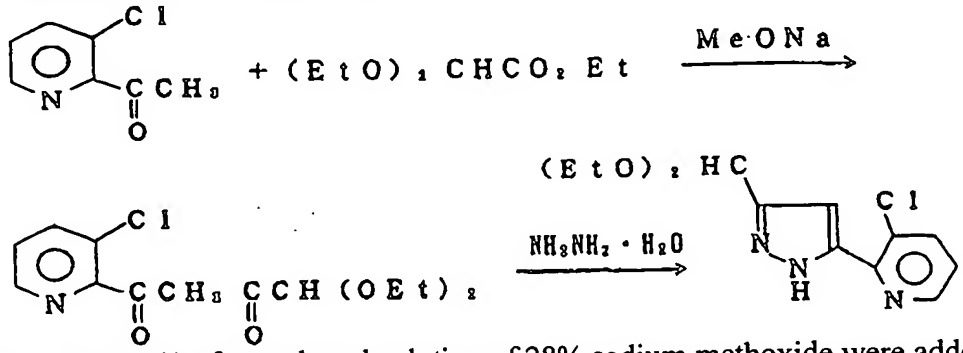


1.8 g (7.0 mmol) of 4,4,4-trifluoro-1-(5-cyclopropyl-2-pyridyl)butane-1,3-dione were dissolved in 15 mL of acetic acid, then 0.42 g (8.4 mmol) of hydrazine hydrate was added, and it

was heated for 15 min at 90-95°C. After the reaction was completed, it was poured into ice water, the precipitated crystals were filtered, and 1.3 g of the target substance was obtained. The total yield beginning with Reference Example 5 was 67%.
Melting point: 152-153°C.

Application Example 11

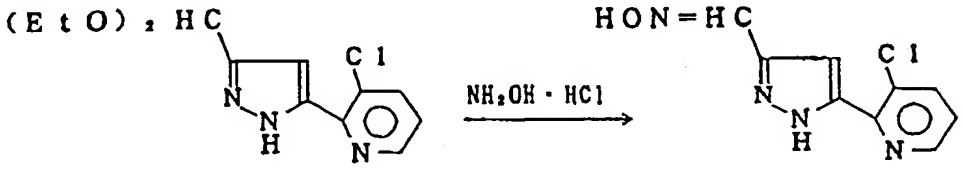
Manufacture of 3-diethoxymethyl-5-(3-chloro-2-pyridyl)pyrazole



9.92 g (51.4 mL) of a methanol solution of 28% sodium methoxide were added under ice-cooling to a 30 mL THF solution of 5.00 g (32.1 mmol) of 3-chloro-2-acetylpyridine and 6.80 g (38.6 mmol) diethoxyethyl acetate, and it was stirred as is for 2.5 h. Next 1.36 g (7.72 mmol) of diethoxyethyl acetate, and 1.98 g (10.3 mmol) of a methanol solution of 28% sodium methoxide were added under ice-cooling, and it was stirred for an additional 17 h at room temperature. 3.70 g of acetic acid were added to the reaction liquid, and after condensation under reduced pressure, water and ethyl acetate were added to the residue, and the liquids were separated. The organic layer was washed with saturated salt water, and after drying over anhydrous magnesium sulfate, the solvent was distilled off, and 10.57 g of a crude 1,3-diketone were obtained. 7.71 g of this crude product were dissolved in 100 mL of ethanol, and under ice-cooling, 1.29 g (25.8 mmol) of hydrazine hydrate were added, and it was stirred for 4.5 h under ice-cooling. The solvents, etc., were distilled off and removed from the reaction liquid under reduced pressure, water was added to the residue, and it was extracted first with chloroform, then with ethyl acetate. Together with the organic layer, it was dried over anhydrous magnesium sulfate, then concentrated under reduced pressure, and the resulting residue was purified by silica gel column chromatography (hexane: ethyl acetate = 2:1), and 4.57 g of 3-diethoxymethyl-5-(3-chloro-2-pyridyl)pyrazole were obtained.
69% yield from 3-chloro-2-acetylpyridine.
Refractive index: $n_D^{22.5}$ 1.5598

Application Example 12

Manufacture of 3-hydroxyiminomethyl-5-(3-chloro-2-pyridyl)pyrazole

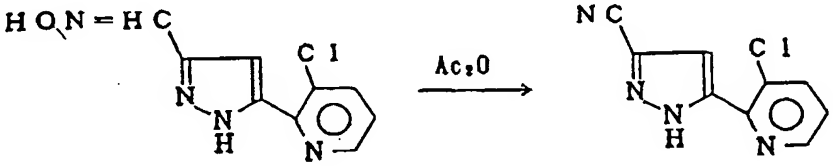


1.50 g (5.32 mmol) of 3-diethoxymethyl-5-(3-chloro-2-pyridyl)pyrazole were dissolved in 20 mL of ethanol, then 0.74 g (10.6 mmol) of hydroxyamine hydrochloride was added, and it was heated and refluxed for 4 h. Sodium hydrogencarbonate was added to the reaction liquid, and after extracting with chloroform and ethyl acetate, it was dried over anhydrous magnesium sulfate. After distilling off the solvent under reduced pressure, the residue was washed with n-hexane, and 0.77 g of 3-hydroxyiminomethyl-5-(3-chloro-2-pyridyl)pyrazole (isomeric mixture) crystals was obtained. 65% yield.

Melting point: 214-216°C

Application Example 13

Manufacture of 3-cyano-5-(3-chloro-2-pyridyl)pyrazole

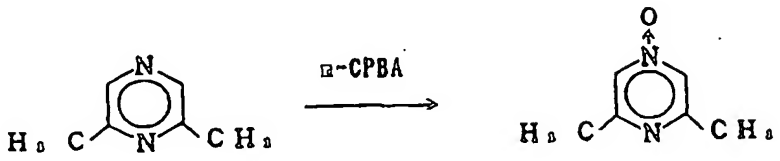


1.30 g (12. 7 mmol) of acetic anhydride were added to 0.57 g (2.56 mmol) of 3-hydroxyiminomethyl-5-(3-chloro-2-pyridyl)pyrazole, and it was heated for 4 h at 110°C. After the reaction mixture was concentrated under reduced pressure, ethanol was added to the residue, and it was concentrated under reduced pressure again. This process was repeated 2 times, then the residue was suspended in 15 mL of ethanol, 2.8 mL (2.8 mmol) of an aqueous solution of 1N sodium hydroxide was added, and it was stirred for 2 h under ice-cooling. Salt water was added to the reaction liquid, and it was extracted with ethyl acetate. After drying the organic layer over anhydrous magnesium sulfate, it was concentrated under reduced pressure. It was crystallized by washing the residue with n-hexane, and 0.40 g of 3-cyano-5-(3-chloro-2-pyridyl)pyrazole was obtained. 77% yield.

Melting point: 204-205°C

Reference Example 6

Manufacture of 2,6-dimethylpyrazine-4-oxide

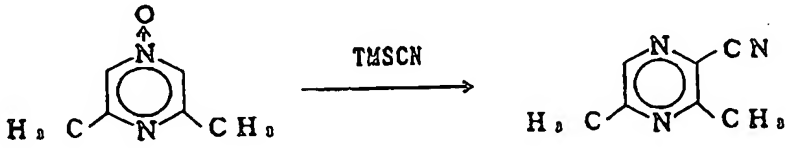


7.23 g (66.9 mmol) of 2,6-dimethylpyrazine were dissolved in 70 mL of chloroform, and under ice-cooling, 15.88 g (73.6 mmol) of 80% pure m-chloroperbenzoic acid were added, and it was stirred overnight at room temperature. After the reaction was completed, the precipitated crystals were filtered, the filtrate was washed with an aqueous solution of sodium hydrogencarbonate, then after drying and concentrating under reduced pressure, 6.43 g of crude 2,6-dimethylpyrazine-4-oxide were obtained.

^{1}H-NMR (CDCl$_3$, δ ppm) : 2.49 (s, 6H), 7.86 (s 2H)

Reference Example 7

Manufacture of 3-cyano-2,6-dimethylpyrazine

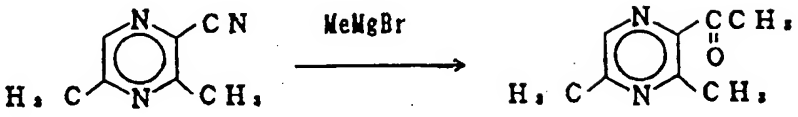


6.20 g (50 mmol) of the 2,6-dimethylpyrazine-4-oxide obtained in Reference Example 6, and 10.1 g (100 mmol) of triethylamine were dissolved in 50 mL of acetonitrile. Then 15.67 g (158.3 mmol) of trimethylsilylcyanide were added, and it was heated and refluxed overnight. After the reaction liquid was cooled, an aqueous solution of sodium carbonate was added, then following concentration under reduced pressure, water and chloroform were added and the liquids were separated. The chloroform layer was dried, and then concentrated under reduced pressure, and the residue obtained was purified by silica gel column chromatography, and 1.60 g of the target substance were obtained. The total yield beginning from Reference Example 6 was 19%.

^{1}H−NMR (CDCl$_3$, δ ppm) : 2.65 (s, 3H), 2.79 (s 3H), 8.42 (s, 1H)

Reference Example 8

Manufacture of 3-acetyl-2,6-dimethylpyrazine



1.52 g (11.4 mmol) of 3-cyano-2,6-dimethylpyrazine were dissolved in 25 mL of dry THF, and under ice-cooling, in a nitrogen gas atmosphere, 4.0 mL (12 mmol) of 3.0M methylmagnesium bromide-diethyl ether solution were added dropwise. After cooling under ice and stirring for an additional 2 h, 1 mL of a saturated aqueous solution of ammonium chloride was added to the reaction liquid, then 5 mL of 4N hydrochloric acid were added, at it was stirred for 2 h. The reaction mixture was concentrated under reduced pressure, and the majority of the THF was removed. Chloroform and a saturated aqueous solution of sodium hydrogencarbonate were added to the residue, and after separating the liquids, the organic layer was dried and concentrated, and a crude product was obtained. This was purified by silica gel column chromatography, and 0.30 g of the target oily substance was obtained. Yield 17%.

^{1}H−NMR (CDCl$_3$, δ ppm) : 2.60 (s, 3H), 2.70 (s 3H), 2.81 (s, 3H), 8.34 (s, 1H)

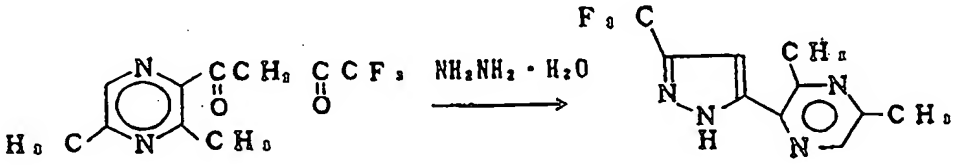
Reference Example 9

Manufacture of 1-(3,5-dimethyl-2-pyrazinyl)-4,4,4-trifluorobutane-1,3-dione

0.30 g (20 mmol) of the product obtained in Reference Example 8 and 0.34 g (24 mmol) of trifluoroethyl acetate were dissolved in 30 mL of THF. Then 0.46 g (24 mmol) of a 28% methanol solution of sodium methoxide was added to this and it was stirred for 15 min at room temperature. 1 mL of acetic acid was added to the reaction liquid, and when the reaction was completed, the reaction mixture was concentrated under reduced pressure, and the majority of the THF was removed. Chloroform and saturated aqueous sodium carbonate were added to the residue, the liquids were separated, the chloroform layer was dried, then concentrated under reduced pressure, and 0.30 g of an oily crude product was obtained. Without further purification, this product was used in the following reaction.

Application Example 14

Manufacture of 3-trifluoromethyl-5-(3,5-dimethyl-2-pyrazinyl)pyrazole



0.30 g (12.2 mmol) of the crude product obtained in Reference Example 9 was dissolved in 5 mL of acetic acid, then 0.09 g (18.3 mmol) of hydrazine hydrate was added to this, and the reaction mixture was heated and refluxed for 2 h. After cooling the reaction liquid, the reaction mixture was poured into water. Then chloroform and a saturated aqueous solution of sodium hydrogencarbonate were added, and the liquids were separated. The organic layer was dried and concentrated, whereby 0.30 g of the target substance was obtained. The total yield beginning from Reference Example 9 was 65%.

Melting point: 175-177°C.

Application Example 15

Manufacture of nickel(II) salt of 5-(5-ethyl-2-pyridyl)-3-trifluoromethylpyrazole

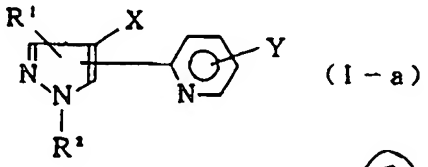
1.4 g (5.81 mmol) of 5-(5-ethyl-2-pyridyl)-3-trifluoromethylpyrazole were dissolved in 15 mL of acetone, then a mixture comprised of 0.38 g (2.41 mL) of nickel(II) chloride dissolved in 30 mL of water was gradually added to this. After stirring at room temperature for 3 h, the precipitated crystals were filtered, washed with 50 mL of water, and 0.6 g of the target substance was obtained. The yield was 38%.

Melting point: 180-185°C

MS m/z: 538 (M + 1)

Representative examples of the compounds of the present invention, including the application examples noted above, are shown in Tables 1-1 and 1-2.

Table 1-1



(I－a)

化合物No.	R^1	Y	X	R^2	置換位置	物理恒数 (℃)
Ia－1	CF_3	H	H	H	3-R^1	[126-127]
Ia－2	CF_3	H	H	銅（II）塩	3-R^1	>260
Ia－3	CF_3	H	NO_2	H	3-R^1	[149-150]
Ia－4	CF_3	H	Br	H	3-R^1	[156-157]
Ia－5	CF_3	H	Br	銅（II）塩	3-R^1	>250
Ia－6	CF_3	H	NO_2	銅（II）塩	3-R^1	>250
Ia－7	CF_3	H	NH_2	H	3-R^1	[123-124]
Ia－8	C_2F_5	H	H	H	3-R^1	[170-175]
Ia－9	C_2F_5	H	H	銅（II）塩	3-R^1	>250
Ia－10	CF_3	6-CH_3	H	H	3-R^1	[148-150]
Ia－11	CF_3	6-Cl	H	H	3-R^1	[90-92]
Ia－12	CF_3	H	CH_3	H	3-R^1	[97-98]
Ia－13	CF_3	4-Cl	H	H	3-R^1	[125-127]
Ia－14	CF_3	3-CH_3	H	H	3-R^1	[140-142]
Ia－15	CF_3	5-CH_3	H	H	3-R^1	[150-151]
Ia－16	CF_3	5-Ph	H	H	3-R^1	[167-169]

Key: 1 Compound No.
2 Substitution site
3 Physical constant (°C)
4 Cupric salt

(A)

表 1－1（続き）

(1) 化合物No.	R^1	Y	X	R^2	(2) 置換位置	(3) 物理恒数 (℃)
Ia－17	CF_3	3,5-$(CH_3)_2$	H	H	3-R^1	[125-126]
Ia－18	CF_3	4-CH_3	H	H	3-R^1	[163-165]
Ia－19	CF_3	4,5-$(CH_3)_2$	H	H	3-R^1	[188-189]
Ia－20	CF_3	3,4-$(CH_3)_2$	H	H	3-R^1	[124-125]
Ia－21	CF_3	5-C_2H_5	H	H	3-R^1	[128-130]
Ia－22	CF_3	5-NO_2	H	H	3-R^1	[150-151]
Ia－23	CF_3	5-Cl	H	H	3-R^1	[136-137]
Ia－24	CF_3	5-Br	H	H	3-R^1	[144-145]
Ia－25	CF_3	5-OCH_3	H	H	3-R^1	[169-170]
Ia－26	CF_3	5-CH_2Ph	H	H	3-R^1	[121-124]
Ia－27	CF_3	5-CN	H	H	3-R^1	[163-168]
Ia－28	CF_3	5-CF_3	H	H	3-R^1	[155-160]
Ia－29	CF_3	3-CF_3	H	H	3-R^1	[109-110]
Ia－30	CF_3	3-Ph	H	H	3-R^1	[130-131]
Ia－31	CF_3	3-CH_2Ph	H	H	3-R^1	[145-150]
Ia－32	CF_3	3-Br	H	H	3-R^1	[122-124]
Ia－33	CF_3	3-Cl	H	H	3-R^1	[120-122]
Ia－34	CF_3	3,6-$(CH_3)_2$	H	H	3-R^1	[158-160]
Ia－35	CF_3	3-C_2H_5	H	H	3-R^1	[103-104]
Ia－36	CF_3	3-$N(CH_3)_2$	H	H	3-R^1	[85-88]
Ia－37	CF_3	5-$C_3H_7^n$	H	H	3-R^1	[79-82]
Ia－38	CF_3	3-$C_3H_7^n$	H	H	3-R^1	[111-112]

[Key to previous page:]

A Table 1-1 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)

表 1－1（続き）

化合物No.	R^1	Y	X	R^2	置換位置	物理恒数 (℃)
Ia－39	CF_3	3-$CH(C_2H_5)_2$	H	H	3-R^1	$n_D^{18.8}$ 1.5122
Ia－40	CF_3	5,6-$(CH_3)_2$	H	H	3-R^1	[165-167]
Ia－41	CF_3	5-$C_4H_9^n$	H	H	3-R^1	[70-72]
Ia－42	CF_3	5-$C_3H_7^i$	H	H	3-R^1	[94-95]
Ia－43	CF_2H	5-C_2H_5	H	H	3-R^1	[121-122]
Ia－44	CF_3	5-NH_2	H	H	3-R^1	[178-180]
Ia－45	CF_2-Cl	5-C_2H_5	H	H	3-R^1	[119-120]
Ia－46	CHFCl	5-C_2H_5	H	H	3-R^1	[111-113]
Ia－47	CF_3	3,5-Cl_2	H	H	3-R^1	[138-140]
Ia－48	CF_3	3-CH_3-5-C_2H_5	H	H	3-R^1	[117-119]
Ia－49	CF_3	3-CH_3-5-$C_3H_7^n$	H	H	3-R^1	
Ia－50	CF_3	3,5-$(C_2H_5)_2$	H	H	3-R^1	[91-93]
Ia－51	CF_3	3-$CH_2CH=CH_2$	H	H	3-R^1	[81-84]
Ia－52	CF_3	5-$CH_2CH=CH_2$	H	H	3-R^1	[97-98]
Ia－53	CF_3	3-SCH_3	H	H	3-R^1	[161-163]
Ia－54	CF_3	5-SCH_3	H	H	3-R^1	[169-171]
Ia－55	CF_3	3-SO_2CH_3	H	H	3-R^1	
Ia－56	CF_3	5-SO_2CH_3	H	H	3-R^1	[220-221]
Ia－57	CF_3	3-CO_2CH_3	H	H	3-R^1	
Ia－58	CF_3	5-CO_2CH_3	H	H	3-R^1	[179-180]
Ia－59	CF_3	5-$CO_2C_2H_5$	H	H	3-R^1	[174-176]
Ia－60	CF_3	3-CH_2OCH_3	H	H	3-R^1	[105-107]

[Key to previous page:]

A Table 1-1 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)

表 1－1（続き）

化合物No.	R^1	Y	X	R^2	置換位置	物理恒数 (℃)
Ia－61	CF_3	5-CH_2OCH_3	H	H	3-R^1	[133-134]
Ia－62	CF_3	3-Cl-5-C_2H_5	H	H	3-R^1	
Ia－63	CF_3	3-OCH_3	H	H	3-R^1	[124-126]
Ia－64	CF_3	5-OC_2H_5	H	H	3-R^1	[165-167]
Ia－65	CF_3	5-$C(CH_3)_3$	H	H	3-R^1	
Ia－66	CF_3	5-CHC_2H_5 (CH$_3$)	H	H	3-R^1	
Ia－67	CF_3	5-$CH_2CH(CH_3)_2$	H	H	3-R^1	
Ia－68	CF_3	3-CH_3-5-OCH_3	H	H	3-R^1	[164-167]
Ia－69	CF_3	3-$CH_2C{\equiv}CH$	H	H	3-R^1	
Ia－70	CF_3	5-$CH_2C{\equiv}CH$	H	H	3-R^1	
Ia－71	CF_3	5-$CHOCH_3$ (CH$_3$)	H	H	3-R^1	
Ia－72	CF_3	3-$CH_2SO_2CH_3$	H	H	3-R^1	
Ia－73	CF_3	5-$CH_2SO_2CH_3$	H	H	3-R^1	
Ia－74	CF_3	5- 	H	H	3-R^1	
Ia－75	CF_3	3-$COCH_3$	H	H	3-R^1	[89-91]
Ia－76	CF_3	5-$COCH_3$	H	H	3-R^1	[200-201]
Ia－77	CO_2CH_3	5-C_2H_5	H	H	3-R^1	[130-133]
Ia－78	CO_2H	5-C_2H_5	H	H	3-R^1	

[Key to previous page:]

A Table 1-1 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)

表 1－1（続き）

化合物No.	R^1	Y	X	R^2	置換位置	物理定数 (℃)
Ia－79	CN	3,5-Cl_2	H	H	3-R^1	[206-207]
Ia－80	CN	3,5-$(CH_3)_2$	H	H	3-R^1	[218-219]
Ia－81	CN	5-C_2H_5	H	H	3-R^1	[183-185]
Ia－82	$CONH_2$	5-C_2H_5	H	H	3-R^1	
Ia－83	NH_2	5-C_2H_5	H	H	3-R^1	
Ia－84	SCH_3	5-C_2H_5	H	H	3-R^1	
Ia－85	SO_2CH_3	5-C_2H_5	H	H	3-R^1	
Ia－86	CF_3	5-C_2H_5	H	CH_2OCCH_3 (O)	3-R^1	$n_D^{20.7}$ 1.5060
Ia－87	CF_3	5-C_2H_5	H	CH_2OCCH_3 (O)	5-R^1	$n_D^{20.7}$ 1.5018
Ia－88	CF_3	5-C_2H_5	H	$CH_2OCC_2H_5$ (O)	3-R^1	
Ia－89	CF_3	5-C_2H_5	H	$CH_2OCC_2H_5$ (O)	5-R^1	
Ia－90	CF_3	5-C_2H_5	H	COPh	3-R^1	
Ia－91	CF_3	5-C_2H_5	H	COPh	5-R^1	
Ia－92	CF_3	5-C_2H_5	H	CO-(C6H4)-Cl	3-R^1	[78-84]
Ia－93	CF_3	5-C_2H_5	H	CO-(C6H4)-Cl	5-R^1	
Ia－94	CF_3	5-C_2H_5	H	CH_2SCH_3	3-R^1	$n_D^{20.6}$ 1.5276

[Key to previous page:]

A Table 1-1 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)

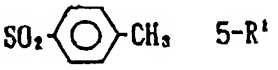
表 1－1（続き）

化合物No.	R^1	Y	X	R^2	置換位置	物理恒数 (℃)
Ia－95	CF_3	5-C_2H_5	H	CH_2SCH_3	5-R^1	$n_D^{20.9}$ 1.5240
Ia－96	CF_3	5-C_2H_5	H	$COCH_3$	3-R^1	[35-37]
Ia－97	CF_3	5-C_2H_5	H	$COCH_3$	5-R^1	^{1}H-NMR 1.33(3H. t) 2.75(2H. d) 2.78(3H. s) 6.8(1H. s) 7.42(1H. d) 7.63(1H. dd) 8.51(1H. d)
Ia－98	CF_3	5-C_2H_5	H	SO_2CH_3	3-R^1	^{1}H-NMR 1.3(3H. t) 2.72(2H. q) 3.44(3H. s) 7.56(1H. s) 7.64(1H. dd) 8.04(1H. d) 8.50(1H. d)
Ia－99	CF_3	5-C_2H_5	H	SO_2CH_3	5-R^1	[100-102]
Ia-100	CF_3	5-C_2H_5	H	CH_2SOCH_3	3-R^1	[88-92]
Ia-101	CF_3	5-C_2H_5	H	$CH_2SO_2CH_3$	3-R^1	[114-116]
Ia-102	CF_3	H	H	$CH_2OC_2H_5$	5-R^1	n_D^{25} 1.4829
Ia-103	CF_3	H	H	$CH_2OC_2H_5$	3-R^1	
Ia-104	CF_3	5-C_2H_5	H	CH_2OC(=O)-C$_6$H$_5$	3-R^1	
Ia-105	CF_3	5-C_2H_5	H	CH_2OC(=O)-C$_6$H$_5$	5-R^1	
Ia-106	CF_3	5-C_2H_5	H	$CH_2OCOC_2H_5$	3-R^1	
Ia-107	CF_3	5-C_2H_5	H	$CH_2OCOC_2H_5$	5-R^1	
Ia-108	CF_3	5-C_2H_5	H	SO_2-C$_6$H$_4$-CH_3	3-R^1	

[Key to previous page:]

A Table 1-1 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)

表 1－1（続き）

化合物No	R^1	Y	X	R^2	置換位置	物理恒数 (℃)
Ia-109	CF_3	5-C_2H_5	H		5-R^1	
Ia-110	CF_3	5-C_2H_5	H	CH_2NCOCH_3 | CH_3	3-R^1	
Ia-111	CF_3	5-C_2H_5	H	CH_2NCOCH_3 | CH_3	5-R^1	
Ia-112	CF_3	5-C_2H_5	H	S ‖ $CH_2SCN(CH_3)_2$	3-R^1	
Ia-113	CF_3	5-C_2H_5	H	S ‖ $CH_2SCN(CH_3)_2$	5-R^1	
Ia-114	CF_3	5-C_2H_5	Cl	H	3-R^1	[179-181]
Ia-115	CF_3	5-C_2H_5	Br	H	3-R^1	[181-182]
Ia-116	CF_3	5-C_2H_5	F	H	3-R^1	[166-168]
Ia-117	CF_3	5-CH=$CHCH_3$	H	H	3-R^1	[153-155]
Ia-118	CF_3	3-CH=CH-CH_3	H	H	3-R^1	[116-117]
Ia-119	CF_3	3-CH=CH_2	H	H	3-R^1	[104-105]
Ia-120	CF_3	5-CH=CH_2	H	H	3-R^1	[113-114]
Ia-121	CF_3	3-Cl-5-$C_3H_7^i$	H	H	3-R^1	
Ia-122	CF_3	3-CH_3-5-$C_3H_7^i$	H	H	3-R^1	
Ia-123	CF_3	5-$C(CH_3)_2OH$	H	H	3-R^1	[58-61]
Ia-124	CF_3	3-C ≡CH	H	H	3-R^1	[140-141]
Ia-125	CF_3	5-C ≡CH	H	H	3-R^1	[167-169]

[Key to previous page:]

A Table 1-1 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)

表 1－1（続き）

化合物No.	R^1	Y	X	R^2	置換位置	物理恒数 (℃)
Ia-126	CF_3	3-CN	H	H	3-R^1	[150-151]
Ia-127	CF_3	5-CH_2CN	H	H	3-R^1	
Ia-128	CF_3	5-SCN	H	H	3-R^1	
Ia-129	CF_3	3-SCN	H	H	3-R^1	
Ia-130	CF_3	3-F	H	H	3-R^1	[119-121]
Ia-131	CF_3	5-F	H	H	3-R^1	
Ia-132	CF_3	3,5-F_2	H	H	3-R^1	
Ia-133	CF_3	3-Cl-5-F	H	H	3-R^1	
Ia-135	CF_3	3-F-5-Cl	H	H	3-R^1	
Ia-136	CF_3	3-Br-5-C_2H_5	H	H	3-R^1	[132-134]
Ia-137	CF_3	3-F-5-CH_3	H	H	3-R^1	
Ia-138	CF_3	3-Cl-5-CH_3	H	H	3-R^1	[152-153]
Ia-139	CF_3	3-Br-5-CH_3	H	H	3-R^1	[150-152]
Ia-140	CF_3	3-F-5-C_2H_5	H	H	3-R^1	
Ia-141	CF_3	3-Cl-5-C_3H_7	H	H	3-R^1	
Ia-142	CF_3	3-Br-5-C_3H_7	H	H	3-R^1	
Ia-143	CF_3	3-F -5-C_3H_7	H	H	3-R^1	
Ia-144	CF_3	3-Cl-5-C_3H_7	H	H	3-R^1	
Ia-145	CF_3	3-Br-5-C_3H_7	H	H	3-R^1	
Ia-146	CF_3	3-Cl-5-C_4H_9	H	H	3-R^1	
Ia-147	CF_3	3-Br-5-C_4H_9	H	H	3-R^1	
Ia-148	CF_3	3-Cl-5-C_4H_9	H	H	3-R^1	

[Key to previous page:]

A Table 1-1 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)

(A)

表 1－1（続き）

(1) 化合物No.	R^1	Y	X	R^2	(2) 置換位置	(3) 物理恒数 (℃)
Ia-149	CF_3	5-C_2H_5	H	$CO_2C_2H_5$	3-R^1	$n_D^{20.7}$ 1.5158
Ia-150	CF_3	5-C_2H_5	H	$CH_2OC(=O)-C_4H_9^t$	3-R^1	[47 - 48]
Ia-151	CF_3	5-C_2H_5	H	$CH_2OC(=O)-C_4H_9^i$	5-R^1	$n_D^{21.0}$ 1.4874
Ia-152	CF_3	5-$SOCH_3$	H	H	3-R^1	[194 -196]
Ia-153	CF_3	5-C_2H_5	H	$CH_2OC(=O)$-(4-NO_2-Ph)	5-R^1	[128 -129]
Ia-154	CF_3	5-C_2H_5	H	$CH_2OC(=O)$-(4-NO_2-Ph)	3-R^1	[122 -124]
Ia-155	CF_3	3-Cl	H	CH_2OCCH_3 (=O)	5-R^1	[62 - 64]
Ia-156	CF_3	3-Cl	H	CH_2OCCH_3 (=O)	3-R^1	$n_D^{20.6}$ 1.5195
Ia-157	CF_3	3-CH_3-5-Cl	H	H	3-R^1	[150 -151]
Ia-158	CF_3	5-$CH(F)-CH_3$	H	H	3-R^1	[138 -140]
Ia-159	CF_3	5-$C(Cl)=CH_2$	H	H	3-R^1	[149 -151]

[Key to previous page:]

A Table 1-1 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)

表 1－1（続き）

化合物No.	R^1	Y	X	R^2	置換位置	物理恒数 (℃)
Ia-160	CF_3	3-C(Cl)=CH_2	H	H	3-R^1	[105 -106]
Ia-161	CF_3	5-OCH_2Ph	H	H	3-R^1	[158 -159]
Ia-162	CF_3	5-OH	H	H	3-R^1	[234 -235]
Ia-163	CF_3	5-OC(=O)CH_3	H	H	3-R^1	[163 -165]
Ia-164	CF_3	3-CH(F)-CH_3	H	H	3-R^1	[90 - 91]
Ia-165	CF_3	3-OCH_3-5-Cl	H	H	3-R^1	[152 -153]
Ia-166	CF_3	3-Cl-5-OCH_3	H	H	3-R^1	[191 -192]
Ia-167	CF_3	3-$CH_2OCH_2OCH_3$	H	H	3-R^1	[101 -103]
Ia-168	CF_3	5-$CH_2OCH_2OCH_3$	H	H	3-R^1	[95 -97]
Ia-169	CF_3	5-$OCONHC_2H_5$	H	H	3-R^1	[175 -177]
Ia-170	CF_3	5-C_2H_5	H	銅（II）塩	3-R^1	[250℃up]

[Key to previous page:]

A Table 1-1 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)
4 Cupric salt

表 1－1（続き）

化合物No.	R^1	Y	X	R^2	置換位置	物理恒数 (℃)
Ia-171	CF_3	3-Cl	H	銅（II）塩	3-R^1	[250℃Cup]
Ia-172	CF_3	5-C_2H_5	H	ニッケル（II）塩	3-R^1	[180 -185]
Ia-173	CF_3	5-C_2H_5	H	コバルト（II）塩	3-R^1	[170 -180]
Ia-174	CF_3	5-C_2H_5	H	鉄（II）塩	3-R^1	[250 ℃Cup]
Ia-175	CF_3	3-Cl	H	ニッケル（II）塩	3-R^1	[152 -160]
Ia-176	CF_3	3-Cl	H	鉄（II）塩	3-R^1	[217 -220]
Ia-177	CF_3	3-C≡C-$SiMe_3$	H	H	3-R^1	[122 -123]
Ia-178	CF_3	5-C_2H_5	H	スズ（II）塩	3-R^1	[260 ℃Cup]
Ia-179	CF_3	3-C≡C-CF_3	H	H	3-R^1	
Ia-180	CF_3	3-C≡C-Cl	H	H	3-R^1	[122 -124]
Ia-181	CF_3	3-C(CH_3)=CH_2	H	H	3-R^1	[85 -86]

[Key to previous page:]

A	Table 1-1 (continued)
1	Compound No.
2	Substitution site
3	Physical constant (°C)
4	Cupric salt
5	Nickel(II) salt
6	Cobalt(II) salt
7	Ferric salt
8	Nickel(II) salt
9	Stannic salt

(A)

(1)　表 1－1（続き）　(2)　(3)

化合物No.	R^1	Y	X	R^2	置換位置	物理恒数 (℃)
Ia-182	CF_3	3-CH=CHCl	H	H	3-R^1	
Ia-183	CF_3	3-CH=CHCN (trans)	H	H	3-R^1	[156 -157]
Ia-184	CF_3	3-C(CN)=CH_2	H	H	3-R^1	
Ia-185	CF_3	3-C(CH_3)=N-OCH_3	H	H	3-R^1	[113 -116]
Ia-186	CF_3	3-C(OCH_3)=CH_2	H	H	3-R^1	
Ia-187	CF_3	3-CH=NOH	H	H	3-R^1	[187 -189]
Ia-188	CF_3	3-CH=$NOCH_3$	H	H	3-R^1	[122 -123]
Ia-189	CF_3	3-OCF_3	H	H	3-R^1	
Ia-190	CF_3	3-$OCHF_2$	H	H	3-R^1	[99 -100]
Ia-191	CF_3	5-$OCHF_2$	H	H	3-R^1	[122 -123]
Ia-192	CF_3	3-SCF_3	H	H	3-R^1	

[Key to previous page:]

A Table 1-1 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)

表 1－1（続き）

化合物No.	R^1	Y	X	R^2	置換位置	物理恒数 (℃)-
Ia-193	CF_3	3-CH_2CN	H	H	3-R^1	
Ia-194	CF_3	3- 	H	H	3-R^1	[95 -97]
Ia-195	CF_3	5- 	H	H	3-R^1	[152 -153]
Ia-196	CF_3	3-CO_2CH_3	H	H	3-R^1	
Ia-197	CF_3	3-C≡C-OCH_3	H	H	3-R^1	[140 -141]
Ia-198	CF_3	5-SCF_3	H	H	3-R^1	
Ia-199	CF_3	5-$CHCH_3$ (Cl)	H	H	3-R^1	[123 -124]
Ia-200	CF_3	5-CH_2F	H	H	3-R^1	
Ia-201	CF_3	5-CHF_2	H	H	3-R^1	[161 -162]
Ia-202	CF_3	5-CH_2CH_2F	H	H	3-R^1	[145 -146]
Ia-203	CF_3	3-C≡CH-5-Cl	H	H	3-R^1	
Ia-204	CF_3	3-C≡CH-5-CH_3	H	H	3-R^1	
Ia-205	CF_3	3-Cl-5-CN	H	H	3-R^1	

[Key to previous page:]

A Table 1-1 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)

(A)

表 1－1 (続き)

① 化合物No.	R^1	Y	X	R^2	② 置換位置	③ 物理恒数 (℃)
Ia-206	CF_3	3-OCH_3-5-CH_3	H	H	3-R^1	[117 -123]
Ia-207	CF_3	3,5-$(OCH_3)_2$	H	H	3-R^1	[222 -223]
Ia-208	CF_3	3,5-Cl_2-4-CH_3	H	H	3-R^1	
Ia-209	CF_3	3,5-$(CH_3)_2$-4-Cl	H	H	3-R^1	
Ia-210	CF_3	3,5,6-$(CH_3)_3$	H	H	3-R^1	
Ia-211	CF_3	3,5-$(CH_3)_2$-6-Cl	H	H	3-R^1	
Ia-212	CF_3	3-Cl	CH_3	H	3-R^1	[80 -82]
Ia-213	CF_3	5-C_2H_5	CH_3	H	3-R^1	[104 -106]
Ia-214	CF_3	3-Br	H	$CHOC_2H_5$ | CH_3	3-R^1	※1

※1 ^{1}H-NMR($CDCl_3$, δ ppm):1.19(3H, t), 1.79(3H, d), 3.40-3.57(2H, m), 5.79(1H, q), 7.17(1H, dd), 7.28(1H, s), 8.02(1H, d), 8.63(1H, d)

Ia-215	CF_3	3-Br	H	$CHOC_2H_5$ | CH_3	5-R^1	※2

※2 ^{1}H-NMR($CDCl_3$, δ ppm):1.02(3H, t), 1.78(3H, d), 3.11-3.40(2H, m), 5.60(1H, q), 6.82(1H, s), 7.28(1H, dd), 8.07(1H, d), 8.69(1H, d)

[Key to previous page:]

A Table 1-1 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)

表 1－1（続き）

化合物No.	R^1	Y	X	R^2	置換位置	物理恒数（℃）
Ia-216	CF_3	3-C≡C-Si$(CH_3)_3$	H	$CHOC_2H_5$ CH_3	5-R^1	※3

※3 ^{1}H-NMR($CDCl_3$, δ ppm):0.17(9H, s), 1.02(3H, t), 1.79(3H, d), 3.13-3.31(2H, m), 5.93(1H, q), 7.00(1H, s), 7.31(1H, dd), 7.90(1H, d)

Ia-217	CF_3	3-C≡CH	H	$CHOC_2H_5$ CH_3	5-R^1	※4

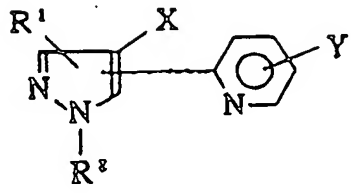
※4 ^{1}H-NMR($CDCl_3$, δ ppm):1.02(3H, t), 1.08(3H, d), 3.14-3.30(2H, m), 3.34(1H, s), 5.93(1H, q), 6.99(1H, s), 7.36(1H, dd), 7.97(1H, d), 8.68(1H, d)

Ia-218	CF_3	3-$SOCH_3$	H	H	3-R^1	[173-174]
Ia-219	CF_3	3-C≡C-CH_3	H	H	3-R^1	[132-134]

[Key to previous page:]

A Table 1-1 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)

表 1－1（続き）



（I－a）

化合物No.	R^1	Y	X	R^2	置換位置	物理恒数（℃）
Ia－220	CF_3	3-CH=NNHCOCH$_3$	H	H	3-R^1	[244-248]
Ia－221	CF_3	3-OCH$_2$Ph	H	H	3-R^1	[154-161]
Ia－222	CF_3	5-C_2H_5	H	H	3-R^1 HCl塩	[194-195]
Ia－223	CF_3	3-Cl	H	H	3-R^1 HCl塩	[157-160]
Ia－224	CF_3	3-CH=CHCO$_2$CH$_3$	H	H	3-R^1	[138-140]
Ia－225	CF_3	3-Cl	H	H	3-R^1 p-TsOH塩	[180-181]
Ia－226	CF_3	3-Cl	H	H	3-R^1 CH_3SO_3H 塩	[163-166]
Ia－227	CF_3	3-Cl	H	H	3-R^1 $(CO_2H)_2$塩	[132-135]
Ia－228	CF_3	5-CH=NOCH$_3$	H	H	3-R^1	[145-147]
Ia－229	CO_2CH_3	3-Cl	H	H	3-R^1	[159-160]
Ia－230	CF_3	3-Cl	Br	H	3-R^1	[111-113]
Ia－231	CF_3	3-C≡CH	H	H	3-R^1 CH_3SO_3H塩	[137-139]
Ia－232	CF_3	3-C≡CH	H	Cu(II) 塩	3-R^1	[148-150]
Ia－233	CF_3	3-C≡CH	H	H	3-R^1 HCl塩	[151-155]
Ia－234	CF_3	5-C(CH$_3$)=NOCH$_3$	H	H	3-R^1	[150-151]
Ia－235	CF_3	5-CH$_2$OH	H	H	3-R^1	[151-152]

[Key to previous page:]

A	Table 1-1 (continued)
1	Compound No.
2	Substitution site
3	Physical constant (°C)
4	HCl salt
5	p-TsOH salt
6	CH_3SO_3H salt
7	$(CO_2H)_2$ salt
8	Cupric salt

表 1－1（続き）

化合物No.	R^1	Y	X	R^2	置換位置	物理恒数 (℃)
Ia－236	CF_3	3,5-Br_2	H	H	3-R^1	[141-143]
Ia－237	CF_3	3-C≡C-CH_2OH	H	H	3-R^1	[134-135]
Ia－238	CF_3	3-C≡CH	H	Ni(II) 塩	3-R^1	[163-165]
Ia－239	SCH_3	3-Cl	H	H	3-R^1	[107-108]
Ia－240	$SOCH_3$	3-Cl	H	H	3-R^1	[134-135]
Ia－241	SO_2CH_3	3-Cl	H	H	3-R^1	[159-161]
Ia－242	CF_3	3- 	H	H	3-R^1	[118-119]
Ia－243	CF_3	3-C≡C-Br	H	H	3-R^1	[140-142]
Ia－244	CF_3	3-CH=CHOCH$_3$ (cis)	H	H	3-R^1	[167-168]
Ia－245	CF_3	3-CH=CHOCH$_3$ (trans)	H	H	3-R^1	[129-130]
Ia－246	OH	H	H	H	3-R^1	[185-190]
Ia－247	CF_3	5-C_2H_5	H	Mn(II) 塩	3-R^1	[250℃up]
Ia－248	OCH_3	H	H	H	3-R^1	[92-93]
Ia－249	CF_3	5-	H	Cu(II) 塩	3-R^1	[260℃up]
Ia－250	CF_3	3-	H	Ni(II) 塩	3-R^1	[185-187]
Ia－251	CF_3	5-	H	Ni(II) 塩	3-R^1	[184-188]
Ia－252	CF_3	3-OSO_2CF_3	H	H	3-R^1	[85-88]
Ia－253	CF_3	5-C_2H_5	CHO	H	3-R^1	[141-143]
Ia－254	CF_3	5-C_2H_5	H	Cu(I) 塩	3-R^1	[250℃up]
Ia－255	CF_3	5-C_2H_5	H	Fe(III) 塩	3-R^1	amorphous
Ia－256	CN	3-Cl	H	H	3-R^1	[204-205]
Ia－257	$CH(OC_2H_5)_2$	3-Cl	H	H	3-R^1	$n_D^{22.5}$ 1.5598

[Key to previous page:]

A Table 1-1 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)
4 Nickel(II) salt
5 Manganese(II) salt
6 Cupric salt
7 Nickel(II) salt
8 Cuprous salt
9 Iron(III) salt

(A)

表 1－1（続き）

化合物No.	R^1	Y	X	R^2	置換位置	物理恒数 (℃)
Ia－258	CH=NOH	3-Cl	H	H	3-R^1	[214-216]
Ia－259	CH=NOCH$_3$ (anti)	3-Cl	H	H	3-R^1	[175-176]
Ia－260	CH=NOCH$_3$ (syn)	3-Cl	H	H	3-R^1	[163-164]
Ia－261	CF_3	5-C_2H_5	H	CH_2OCO--Ph-4-Cl	3-R^1	
Ia－262	CF_3	5-C_2H_5	H	COPh-4-CH_3	3-R^1	
Ia－263	CF_3	3-Cl	H	COPh-4-OCH_3	3-R^1	
Ia－264	CF_3	3-Cl	H	COPh-3-CF_3	3-R^1	
Ia－265	CF_3	3-Cl	H	COPh-4-OCF_3	3-R^1	
Ia－266	CF_3	5-C_2H_5	H	COPh-4-NO_2	3-R^1	
Ia－267	CF_3	3-Cl	H	CH_2OCO--Ph-4-CH_3	3-R^1	
Ia－268	CF_3	3-Cl	H	CH_2OCO--Ph-4-OCH_3	3-R^1	
Ia－269	CF_3	3-Cl	H	CH_2OCO--Ph-3-CF_3	3-R^1	
Ia－270	CF_3	5-C_2H_5	H	CH_2OCO--Ph-4-OCF_3	3-R^1	
Ia－271	CF_3	3-Cl	H	SO_2-Ph	3-R^1	
Ia－272	CF_3	3-Cl	H	SO_2-Ph-4-Cl	3-R^1	
Ia－273	CF_3	3-Cl	H	SO_2-Ph-4-NO_2	3-R^1	
Ia－274	CF_3	5-C_2H_5	H	SO_2-Ph-4-OCH_3	3-R^1	
Ia－275	CF_3	5-C_2H_5	H	SO_2-Ph-3-CF_3	3-R^1	

[Key to previous page:]

A Table 1-1 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)

(1) (4A)

表 1－1（続き）

(2) (3)

化合物No.	R^1	Y	X	R^2	置換位置	物理恒数 (℃)
Ia－276	CF_3	5-C_2H_5	H	SO_2-Ph-4-OCF_3	3-R^1	
Ia－277	CF_3	5-$NHCH_3$	H	H	3-R^1	
Ia－278	CF_3	5-Ph-4-Cl	H	H	3-R^1	
Ia－279	CF_3	5-Ph-4-CH_3	H	H	3-R^1	
Ia－280	CF_3	5-Ph-4-OCH_3	H	H	3-R^1	
Ia－281	CF_3	5-Ph-3-CF_3	H	H	3-R^1	
Ia－282	CF_3	5-Ph-4-OCF_3	H	H	3-R^1	
Ia－283	CF_3	5-Ph-4-NO_2	H	H	3-R^1	
Ia－284	CF_3	5-CH_2-Ph-4-Cl	H	H	3-R^1	
Ia－285	CF_3	5-CH_2-Ph-4-CH_3	H	H	3-R^1	
Ia－286	CF_3	5-CH_2-Ph-4-OCH_3	H	H	3-R^1	
Ia－287	CF_3	5-CH_2-Ph-3-CF_3	H	H	3-R^1	
Ia－288	CF_3	5-CH_2-Ph-4-OCF_3	H	H	3-R^1	
Ia－289	CF_3	5-CH_2-Ph-4-NO_2	H	H	3-R^1	
Ia－290	CN	3-CH_3	H	H	3-R^1	[238-239]
Ia－291	CN	5-CH_3	H	H	3-R^1	[244-246]
Ia－292	CN	3-C_6H_7	H	H	3-R^1	[127-128]
Ia－293	CN	5-C_6H_7	H	H	3-R^1	[120-122]
Ia－294	CN	3-	H	H	3-R^1	[158-160]
Ia－295	CN	5-	H	H	3-R^1	[176-177]
Ia－296	CN	3-Br	H	H	3-R^1	
Ia－297	CF_3	3.5- 	H	H	3-R^1	[128-129]

[Key to previous page:]

A Table 1-1 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)

表 1－1（続き）

化合物No.	R^1	Y	X	R^2	置換位置	物理恒数 (℃)
Ia－298	CN	5-Cl	H	H	3-R^1	[240-241]
Ia－299	CN	3-OCH_3	H	H	3-R^1	[235-238]
Ia－300	CN	5-OCH_3	H	H	3-R^1	
Ia－301	CN	3-CF_3	H	H	3-R^1	[172-174]
Ia－302	CN	5-CF_3	H	H	3-R^1	
Ia－303	CN	3-OCH_3-5-Cl	H	H	3-R^1	[227-228]
Ia－304	CN	3-Cl-5-OCH_3	H	H	3-R^1	
Ia－305	CF_3	5-OCN	H	H	3-R^1	
Ia－306	$CSNH_2$	3-Cl	H	H	3-R^1	[233-234]
Ia－307	$CSNH_2$	5-Cl	H	H	3-R^1	

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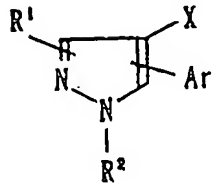
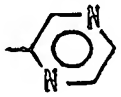
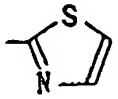
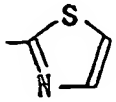
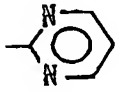
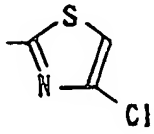
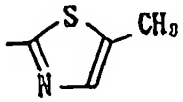
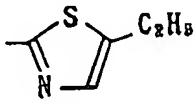
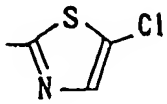
A Table 1-1 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)

表 1－2



(Ib)

化合物No.	R^1	Ar	X	R^2	置換位置	物理恒数
Ib－1	CF_3		H	H	3-R^1	[134-135]
Ib－2	CF_3		H	H	3-R^1	[164-166]
Ib－3	CF_3		H	銅（II）塩	3-R^1	>250
Ib－4	CF_3		H	H	3-R^1	[193-194]
Ib－5	CF_3		H	H	3-R^1	
Ib－6	CF_3		H	H	3-R^1	
Ib－7	CF_3		H	H	3-R^1	
Ib－8	CF_3		H	H	3-R^1	

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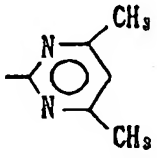
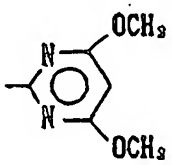
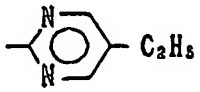
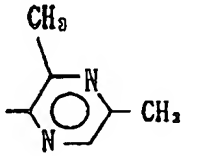
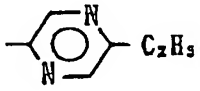
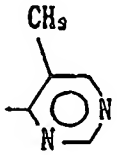
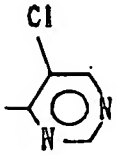
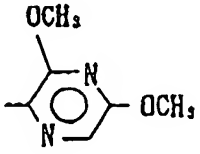
A Table 1-2
1 Compound No.
2 Substitution site
3 Physical constant (°C)
4 Cupric salt

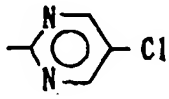
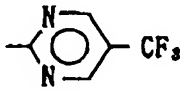
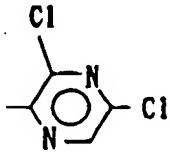
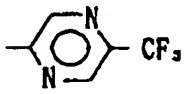
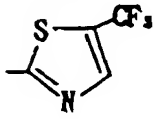
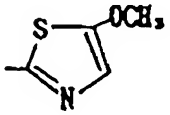
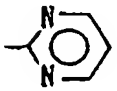
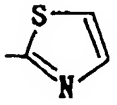
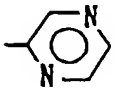
表 1－2（つづき）

化合物No.	R^1	Ar	X	R^2	置換位置	物理恒数
Ib－9	CF_3		H	H	3-R^1	
Ib－10	CF_3		H	H	3-R^1	
Ib－11	CF_3		H	H	3-R^1	
Ib－12	CF_3		H	H	3-R^1	[175-177]
Ib－13	CF_3		H	H	3-R^1	
Ib－14	CF_3		H	H	3-R^1	
Ib－15	CF_3		H	H	3-R^1	
Ib－16	CF_3		H	H	3-R^1	[222-224]

[Key to previous page:]

A Table 1-2 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)

表 1－2（つづき）

化合物No.	R^1	Ar	X	R^2	置換位置	物理恒数
Ib－17	CF_3		H	H	3-R^1	
Ib－18	CF_3		H	H	3-R^1	
Ib－19	CF_3		H	H	3-R^1	
Ib－20	CF_3		H	H	3-R^1	
Ib－21	CF_3		H	H	3-R^1	
Ib－22	CF_3		H	H	3-R^1	
Ib－23	CN		H	H	3-R^1	
Ib－24	CN		H	H	3-R^1	
Ib－25	CF_3		H	H	3-R^1	

[Key to previous page:]

A Table 1-2 (continued)
1 Compound No.
2 Substitution site
3 Physical constant (°C)

Because the compounds of the present invention have an excellent bacetericidal effect against a wide range of filimentous bacteria, they can be used to prevent diseases that occur in the cultivation of agricultural or horticultural plants, including flowering plants and grasses, etc. Examples of diseases the compounds of the present invention can control include the following:

Rice	*Pyricularia oryzae*
	Rhizoctonia solani
	Gibberella fujikuroi
	Cochliobolus miyabeanus
Barley	*Ustilago nuda*
Wheat	*Gibberella zeae*
	Puccinia recondita
	Pseudocercosporella herpotrichoides
	Leptosphaeria nodorum
	Erysiphe graminis f. sp. *tritici*
	Micronectriella nivalis
Potato	*Phytophthora infestans*
Peanut	*Mycosphaerella arachidis*
Sugar beet	*Cercospora beticola*
Cucumber	*Sphaerotheca fuliginea*
	Sclerotinia sclerotiorum
	Botrytis cinerea
	Pseudoperonospora cubensis
Tomato	*Cladosporium fulvum*
	Phytophthora infestans
Eggplant	*Corynespora melongenae*
Onion	*Botrytis allii*
Strawberry	*Sohaerotheca humuli*
Apple	*Podosphaera leucotricha*
	Venturia inaequalis
	Monilinia mali
Persimmon	*Gloeosporium kaki*
Peach	*Monilinia fructicola*
Grape	*Uncinula necator*
	Plasmopara viticola
Japanese pear	*Gymnosporangium asiaticum*

	Alternaria kikuchiana
Tea	*Pestalotia theae*
	Colletotrichum theae-sinensis
Citrus fruit	*Elisinoe fawcetti*
	Pennisillium italicum
Western camellia	*Sclerotinia borealis*

Recently, it has been discovered that various pathogenic bacteria have developed resistance to benzimidazoles, dicarboximides and acylalanine agents. As a result, the effect of these drugs becomes insufficient, and there is a demand for an agent that is effective against resistant types of pathogenic bacteria. Even with sensitive strains, the compounds of the present invention are agents which have an excellent bactericidal effect even against pathogenic bacterial strains that were resistant to benzimidazoles, dicarboximides and acylalanine agents.

Preferred examples of diseases for which the present invention can be applied include *Venturia inaequalis* (apple), *Erysiphe graminis* f. sp. *tritici* (wheat), *Botrytis cinerea* (cucumber), *Plasmopara viticola* (grape), etc.

The compounds of the present invention can also be used as antipollution agents for preventing water-borne microorganisms from adhering to objects that contact the water, such as ships, fish nets, etc.

Moreover, by blending the compounds of the present invention with coatings, fibers, etc., they can be used as antifungal and protective agents for walls and bathtubs as well as shoes and clothing.

Some of the compounds of the present invention display insectidal, miticidal, and herbicidal activities.

Bactericides

The compounds of the present invention produced in this way can be actually used in pure form without the addition of any other component. In addition, when used as agricultural chemicals, which is an object of the present invention, the compounds of the present invention can also be used in a form in which agricultural chemicals are generally used, for example, in the form of a wettable powder, granules, powder, emulsion, water-soluble agent, suspension, a flowable agent, etc. Examples of solid agents that can be used as additives or carriers include vegetable powders such as soy powder, wheat powder, etc.; mineral fine powders such as diatomaceous earth, apatite, gypsum, talc, bentonite, pyrophyllite, clay, etc.; and organic and inorganic compounds such as benzoate soda, urea, Glauber's salt, etc. When used in liquid form, solvents that can be used include petroleum fractions such as kerosene, xylene, solvent naphtha,

etc.; and cyclohexane, cyclohexanone, dimethylformamide, dimethyl sulfoxide, alcohol, acetone, trichloroethylene, methyl isobutyl ketone, mineral oil, vegetable oil, water, etc. Surfactants can be added to these preparations if necessary to provide uniformity and stability to the form.

Such wettable powders, emulsions, and flowable agent can be diluted to a specific concentration with water to create a suspension or emulsion. The powders and granules can be used as is by spreading them on the plants.

Moreover, although the compounds of the present invention display sufficient effect by themselves, they can also be used in combination with one or more other types of bactericide, insecticide, miticide, or agents with combined effects.

Substances that can be mixed with the compounds of the present invention to create bactericides, insecticides, miticides, nematocides, or plant growth regulators are listed below.

Bactericides:

Copper fungicides:

Basic copper chloride, basic copper sulfide, etc.

Sulfur agents:

Thiuram, maneb, mancozeb, polycarbamate, propineb, ziram, and zineb, etc.;

Polyhaloalkylthio agents:

Captan, dichlofluanid, folpet, etc.

Organochlorine agents:

Chlorothalonil, Fusalide, etc.

Organophosphorus agents:

IBP, EDDP, tolclofos methyl, pyrazophos, fosetyl, etc.

Benzimidazole agents:

Thiophanate-methyl, benomyl, carbendazim, thiabendazole, etc.

Dicarboximide agents:

Iprodione, vinclozolin, procymidone, fluorimide, etc.

Carboxamide agents:

Oxycarboxin, mepronil, flutolanil, teclofutram*, triclamide, pencycuron, etc.

Acylalanine agents:

Metalaxyl, oxadixyl, furalaxyl, etc.

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* [Editor's note: An asterisk indicates a transliteration.]

SBI agents:

Triadimefon, triadimenol, Bitertanol, myclobutanyl, hexaconazole, Propiconazole, triflumizole, prochloraz, peflazoate*, Fenarimol, pyrifenox, triforine, flusilazole, etaconazole, diclobutrazol, fluotrimazol*, flutriafen*, penconazol, diniconazole, cyproconazole, imazalil, tridemorph, fenpropimorph, buthiobat, etc.

Antibiotics:

Polyoxin, blasticidin S, casgamycin*, validamycin, dihydrostreptomycin sulfate, etc.

Other:

Propamocarb hydrochloride, Quintozene, hydroxyisooxazole, methasulfocarb, anilazine, isoprothiolane, probenazole, chinomethionate, dithianon, dinocap, dichlomezin, mepanipyrim*, felimuzon*, fluazinam, pyroquilon, tricyclazole, oxolinic* acid, dithianon [sic], iminokutadine* acetate, cymoxanil, pyrolnithrin*, methasulfocarb [sic], diethofencarb, binapacryl, lecithin, sodium bicarbonate, fenaminosulf, dodine, dimethomorph, fenadine oxide, etc.

Insecticide and miticides:

Organophosphorus and carbamate insecticides:

Fenthion, fenitrothion, diazinon, chlorpyriphos, ESP, vamidithion, phenthoate, dimethoate, formothion, marathon, trichlorfon, thiometon, Phosmet, dichloros, acephate, EPBP, methyl parathion, oxydemeton-methyl, ethion, salithion, cyanophos, isoquisathion, pyridaphenthion, phosalone, methidathion, sulprofos, chlorfenvinphos, tetrachlorvinphos, diethylvinphos, propaphos, isofenphos, ethylthiometon*, profenfos, pyraclofos, monocrotophos, azinphos methyl, aldicarb, methomyl, thiodicarb, carbofuran, carbosulfan, benfuracarb, furathiocarb, Propoxur, BPMC, MTMC, MIPC, carbaryl, pirimicarb, ethiofencarb, phenoxycarb, etc.

Pyrethroid insecticides:

Permethrine, cypermethrin, deltamethrin, fenvalerate, Fenpropathrin, pyrethrin, allethrin, tetramethrin, resmethrin, simetryn, propathrin, phenothrin, protrin, fluvalinate, cyfluthrin, cyhalothrin, flucythrinate, ethofenprox, cycloprothrin, tralomethrin, silafluofen, brofenprox*, acrynathli*, etc.

Benzourea and other insecticides:

Diflubenzuron, chlorfurazon*, hexaflumalon, trilumalon, tetrabenzuron, flufenoxuron, flucycloxuron, buprofezin, pyriproxyfine*, methoprene, cartap, thicyclam, bensultap, benzpin*, thiafenthiuron*, acetamprid*, nitenpiram*, imidacloprid, fepronil*, nicotine sulfate, rotenone, metaldehyde, machine oil, BT and microbiological agricultural chemicals such as entopathological viruses, etc.

Nematocides:

Fenamiphos, phosthiazate*, etc.

Miticides:

Chlorobenzilate, fenisobromolate*, Dicofol, amitraz, BPPS, benzomate*, hexythiazox, fenbutatin oxide, polynaktin, chinomethionate, CPCBS, tetradifon, abamectin, milbemectin*, clofentezine, cyhexatin, pyridaben*, fenpyroximate*, tebufenpyrad*, pirimidifen*, fenthiocarb, dienochlor*, etc.

Plant growth regulators:

Divalerins (for example, divalerin A3, divalerin A4, divalerin A7) IAA, NAA.

Application examples

Bactericides

A few application examples of compositions of the present invention are put forth below. The additives and percentages added are not limited to those noted in the application examples, and are widely modifiable.

The term "parts" in the application examples is used to indicate "parts by weight."

Application Example 10 Wettable powder

Compound of the present invention	40 parts
Diatomaceous earth	53 parts
Higher alcohol sulfuric ester	4 parts
Alkyl naphthalene sulfonate	3 parts

A wettable powder containing 40% active ingredient is obtained by uniformly mixing and pulverizing the above.

Application Example 11 Emulsion

Compound of the present invention	30 parts
Xylene	33 parts
Dimethylformamide	30 parts
Polyoxyethylene alkylaryl ether	7 parts

An emulsion containing 30% active ingredient is obtained by mixing and dissolving the above.

Application Example 12 Suspension

Compound of the present invention	10 parts
Sodium lignosulfonate	4 part
Sodium dodecylbenzenesulfonate	1 part
Xantham gum	0.2 parts
Water	84.8 parts

A suspension containing 10% active ingredients is obtained by mixing the above and wet pulverizing to a granularity of 1 μm or less.

Effect of the Invention

Test examples are offered below in which the compounds of the present invention are used as the active ingredients in agents for controlling various plant diseases. The controlling effect was calculated by macroscopic observation of the degree of growth of the diseased spots and fungus apparent on the leaves and roots, etc., during inspections.

Test Example 1 Control test of apple (*Venturia inaequalis*)

An emulsion of a compound of the present invention was scattered at a concentration of 200 ppm of active ingredient on apple seedlings cultivated in an unglazed pot (cultivar: "Kokubei," at 3-4 leaves). After scattering, it was allowed to dry naturally at room temperature, condia of apple *Venturia inaequalis* were sown, and kept for 2 weeks in a room at a constant temperature (20°C) and high humidity in which light and darkness was repeatedly alternated every 12 h. The condition of disease spots on the leaves was inspected and compared to untreated plants to calculate the controlling effect of the agent. The results showed that the compounds noted below had an excellent controlling effect of at least 75%.

Ia-3, 4, 11, 22, 25, 41, 42, 43, 50, 63, 115, 124, 136, 138, 158, 165, 230, 231, 232, 233, 236, 243, 245, 247

Test Example 2 Control test of wheat (*Erysiphe graminis f. sp. tritici*)

An emulsion of a compound of the present invention was scattered at a concentration of 200 ppm of active ingredient on wheat seedlings cultivated in an unglazed pot (cultivar: "Chihoku," at 0.1 to 1.2 leaves). After scattering, it was allowed to dry naturally at room temperature, condia of wheat *Erysiphe graminia f. sp. tritici* were sown, and kept for 7 days in a 22-25°C room. The condition of disease spots on the leaves was inspected and compared to untreated plants to calculate the controlling effect of the agent. The results showed that the compounds noted below had an excellent controlling effect of at least 75%.

Ia-3, 26, 32, 37, 39, 41, 42, 43, 45, 47, 53, 63, 115, 118, 120, 124, 136, 138, 139, 157, 165, 166, 167, 230, 244

Test Example 3 Control test of cucumber (*Botrytis cinerea*)

An emulsion of a compound of the present invention was scattered at a concentration of 200 ppm of active ingredient on cucumber seedlings cultivated in an unglazed pot (cultivar:

"Sagami Semi-white"). After scattering, it was allowed to dry naturally at room temperature, a suspension of condia of cucumber *Botrytis cinerea* was added dropwise onto and sown [sic] on the cucumber leaves, and kept for 4 days in a room in complete darkness at a constant temperature (20°C) and high humidity. The condition of disease spots on the leaves was inspected and compared to untreated plants to calculate the controlling effect of the agent. The results showed that the compounds noted below had an excellent controlling effect of at least 75%.

Ia－1，2，13，14，15，17，20，21，22，23，24，25，28，29，32，33，34，35，36，37，38，39，40，41，42，43，45，46，47，48，50，60，61，63，86，87，94，95，96，98，99，116，117，118，119，120，124，125，130，136，138，139，155，156，157，158，159，160，164，165，166，167，168，170，171，172，173，174，176，177，178，218，222，223，224，225，226，227，228，231，232，233，236，238，239，242，243，244，245，246，247，250，251

Ib－2，4

Test Example 4 Control test of cucumber (*Pseudoperonospora cubensis*)

An emulsion of a compound of the present invention was scattered at a concentration of 200 ppm of active ingredient on cucumber seedlings cultivated in an unglazed pot (cultivar: "Sagami Semi-white"). After scattering, it was allowed to dry naturally at room temperature, a suspension of condia of cucumber *Pseudoperonospora cubensis* was sprayed onto and sown on the cucumbers, and kept for 4 days in a room at a constant temperature (25°C) and dry humidity in which light and darkness was repeatedly alternated every 12 h. The condition of disease spots on the leaves was inspected and compared to untreated plants to calculate the controlling effect of the agent. The results showed that the compounds noted below had an excellent controlling effect of at least 75%.

Ia-2. 4. 17. 20. 21. 24. 32. 37. 39. 41. 42. 43. 45. 47. 118. 120. 136. 138. 139. 157. 170. 236. 243

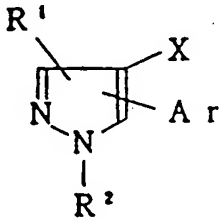
Test Example 5 Control test of grape (*Plasmopara viticola*)

The leaves of field-cultivated grapes (cultivar: "Kohairo," 3 years old) were punched into 30 mm diameter disks, which were then immersed in a liquid containing an emulsion of a compound of the present invention at a concentration of 200 ppm of active ingredient. After immersion, it was allowed to dry naturally at room temperature, and a suspension of zoospores of grape *Plasmopara viticol* was sprayed on and sown, and kept for 10 days in a room at a constant temperature (20°C) under lighted conditions. The condition of disease spots on the leaves was inspected and compared to untreated plants to calculate the controlling effect of the agent. The results showed that the compounds noted below had an excellent controlling effect of at least 75%.

Ia-1. 11. 13. 20. 21. 23. 24. 29. 31. 32. 33. 35. 37. 39. 41. 42. 46. 47. 50. 86. 87. 96. 118. 119. 120. 130. 136. 138. 139. 155. 156. 157. 159. 160. 170. 171. 176. 230. 236. 243. 245. 251. 253

Claims

1. Pyrazole compounds or salts thereof represented by general formula (I-1) (excluding cases wherein R^1 represents CF_3, Ar represents 2-pyridyl, and X and R^2 are both hydrogen atoms):



(I-1)

(where R^1 represents a C_{1-6} haloalkyl group, a C_{1-6} alkoxycarbonyl group, a carboxy group, a cyano group, a C_{1-6} alkylthio group, a C_{1-6} alkylsulfinyl group, a C_{1-6} alkylsulfonyl, C_{1-6} alkoxy group, a C_{1-6} alkoxyiminomethyl group, a C_{1-6} alkoxymethyl group, an amino group, or a carbamoyl group;

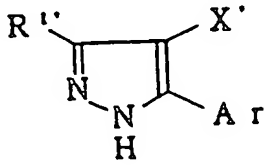
R^2 represents a hydrogen atom, a heavy metal atom, a C_{1-6} alkoxy C_{1-6} alkyl group, a C_{1-6} alkylcarbonyloxymethyl group, a C_{1-6} alkylthiomethyl group, a C_{1-6} alkylsulfinylmethyl group, a C_{1-6} alkylsulfonylmethyl group, a benzoyl group optionally substituted with a (halogen atom, C_{1-6} [C_{1-4}] alkyl group, C_{1-6} alkoxy group, a C_{1-6} haloalkyl group, a C_{1-6} haloalkoxy group, or a nitro group), a C_{1-6} alkylcarbonyl group, a C_{1-6} alkoxycarbonyl group, a C_{1-6} alkylsulfonyl group, a benzoyloxymethyl group optionally substituted with a (halogen atom, C_{1-6} alkyl group, C_{1-6} alkoxy group, a C_{1-6} haloalkyl group, a C_{1-6} haloalkoxy group, or a nitro group), a C_{1-6} alkoxycarbonyloxymethyl group, a phenylsulfonyl group optionally substituted with a (halogen atom, C_{1-6} alkyl group, C_{1-6} alkoxy group, a C_{1-6} haloalkyl group, or a nitro group), an N-C_{1-6} alkyl-N-C_{1-6} alkylcarbonylaminomethyl group, or an N,N-di C_{1-6} alkylthiocarbamoylthiomethyl group;

X represents a hydrogen atom, a halogen atom, a nitro group, amino group, formyl group, or a C_{1-6} alkyl group;

Ar represents a 2-pyridyl group optionally substituted (with a hydrogen atom; a C_{1-6} alkyl group (optionally substituted with a halogen atom, C_{1-6} alkoxy group, hydroxy group, C_{1-6} alkylsulfonyl group, cyano group, hydroxyimino group, C_{1-6} alkoxyimino group, C_{1-6} alkylcarbonylhydrazino group, C_{1-6} alkoxycarbonyl group, or C_{1-4} alkoxy C_{1-4} alkoxy group); C_{2-6} alkenyl group (optionally substituted with a halogen atom, cyano group, C_{1-6} alkoxycarbonyl group, or C_{1-6} alkoxy group); a C_{2-6} alkynyl group (optionally substituted with a halogen atom, a trimethylsilyl group, a hydroxy group, or a C_{1-6} alkoxy group); a mono C_{1-3} alkylamino group; a di C_{1-3} alkylamino group; an amino group; a C_{1-6} alkylthio group optionally substituted with a halogen atom; a C_{1-6} alkylsulfonyl group; a C_{1-6} alkylsulfinyl

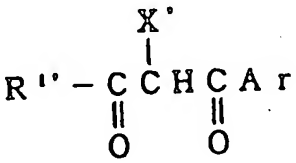
group; a C_{1-6} alkoxycarbonyl group; a C_{3-6} cycloalkyl group, C_{1-6} alkylcarbonyl group, cyanate group, thiocyanate group; a C_{1-6} alkoxy group optionally substituted with a halogen atom; a benzyloxy group; hydroxy group; C_{1-6} alkycarbonyloxy group, C_{1-6} alkycarbamoyloxy group, C_{1-6} haloalkylsulfonyloxy group; a 1-2-epoxy C_{2-6} alkyl group, nitro group; a phenyl group (optionally substituted with a halogen atom, C_{1-6} alkyl group, C_{1-6} alkoxy group, C_{1-6} haloalkyl group, C_{1-6} haloalkoxy group, or nitro group); or a benzyl group (optionally substituted with a halogen atom, a C_{1-6} alkyl group, a C_{1-6} alkoxy group, a C_{1-6} haloalkyl group, a C_{1-6} haloalkoxy group, or a nitro group)); a 2-pyrimidinyl group (optionally substituted with a halogen atom, C_{1-6} alkyl group, C_{1-6} alkoxy group, C_{1-6} haloalkyl group); a 2-pyrazinyl group (optionally substituted with a halogen atom, C_{1-6} alkyl group, C_{1-6} alkoxy group, C_{1-6} haloalkyl group); or a 2-thiazolyl group (optionally substituted with a halogen atom, C_{1-6} alkyl group, C_{1-6} alkoxy group, C_{1-6} haloalkyl group).

2. A method for manufacturing a pyrazole compound expressed by formula (I-3):



(I − 3)

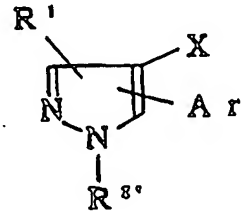
(where $R^{1'}$ represents a C_{1-6} haloalkyl group, a C_{1-6} alkoxycarbonyl group, or a C_{1-6} alkoxymethyl group; X' represents a hydrogen atom or a C_{1-6} alkyl group, and Ar has the same meaning described above), which is characterized in that hydrazine is reacted with a β-diketone represented by formula (II):



(II)

(where $R^{1'}$, X' and Ar have the same meanings described above).

3. A method for manufacturing a pyrazole compound expressed by formula (I-9):



(I − 9)

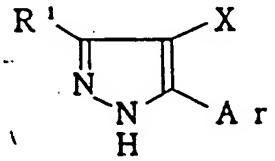
(where R^1 X, and Ar have the same meanings described above, and $R^{2'}$ represents a C_{1-6} alkoxy C_{1-6} alkyl group, a C_{1-6} alkylcarbonyloxymethyl group, a C_{1-6} alkylthiomethyl group, a C_{1-6} alkylsulfonylmethyl group, a benzoyl group optionally substituted with a (halogen atom, C_{1-6} alkyl group, C_{1-6} alkoxy group, a C_{1-6} haloalkyl group, C_{1-6} haloalkoxy group, or a nitro group), a C_{1-6} alkylcarbonyl group, a C_{1-6} alkoxycarbonyl group, a C_{1-6} alkylsulfonyl group, a benzoyloxymethyl group optionally substituted with a (halogen atom, C_{1-6} alkyl group, C_{1-6} alkoxy group, a C_{1-6} haloalkyl group, C_{1-6} haloalkoxy group, or a nitro group), a C_{1-6} alkoxycarbonyloxymethyl group, a phenylsulfonyl group optionally substituted with a (halogen atom, C_{1-6} alkyl group, C_{1-6} alkoxy group, a C_{1-6} haloalkyl group, a C_{1-6} haloalkoxy group, or a nitro group), an N-C_{1-6} alkyl-N-C_{1-6} alkylcarbonylaminomethyl group, or a N,N-di C_{1-6} alkylthiocarbamoylthiomethyl group)

which is characterized by reacting a compound expressed by formula (IV)

$$R^{2'}V \qquad (IV)$$

(where $R^{2'}$ has the same meanings described above, and V represents a halogen atom);

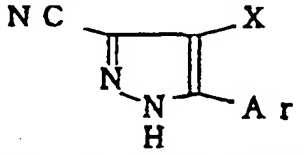
and a compound expressed by formula (I-5):



(I − 5)

(where R^1, Ar, and X have the same meanings described above).

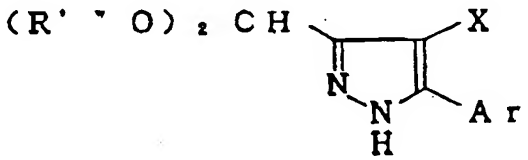
4. A method for manufacturing a pyrazole compound expressed by formula (I-12):



(I − 12)

(where X and Ar have the same meanings described above);

which is characterized in that a hydroxyamine is reacted with a compound expressed by the formula (I-10):



(I − 10)

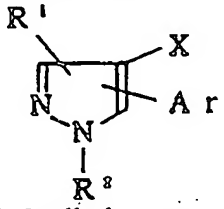
(where X and Ar have the same meanings described above, and R' " represents a C_{1-6} alkyl group);

and reacting the compound created that can be expressed by the formula (I-11):

(I－11)

(where X and Ar have the same meanings described above) with an acid anhydride.

5. An agrohorticultural bactericide containing, as an effective ingredient, 1 or 2 or more of the pyrazole compounds or salts thereof expressed by formula (I-2):



(I－2)

(where R^1 represents a C_{1-6} haloalkyl group, a C_{1-6} alkoxycarbonyl group, a carboxy group, a cyano group, a C_{1-6} alkylthio group, a C_{1-6} alkylsulfinyl group, a hydroxy group, a hydroxyiminomethyl group, a C_{1-6} alkoxyiminomethyl group, a C_{1-6} di-alkoxymethyl group, a C_{1-6} alkoxy group, a thiocarbamoyl group, a C_{1-6} alkylsulfonyl group, an amino group, or a carbamoyl group;

R^2 represents a hydrogen atom, a heavy metal atom, a C_{1-6} alkoxy C_{1-6} alkyl group, a C_{1-6} alkylcarbonyloxymethyl group, a C_{1-6} alkylthiomethyl group, a C_{1-6} alkylsulfinylmethyl group, a C_{1-6} alkylsulfonylmethyl group, a benzoyl group optionally substituted with a (halogen atom, C_{1-6} alkyl group, C_{1-6} alkoxy group, a C_{1-6} haloalkyl group, a C_{1-6} haloalkoxy group, or a nitro group), a C_{1-6} alkylcarbonyl group, a C_{1-6} alkoxycarbonyl group, a C_{1-6} alkylsulfonyl group, a benzoyloxymethyl group optionally substituted with a (halogen atom, C_{1-6} alkyl group, C_{1-6} alkoxy group, a C_{1-6} haloalkyl group, a C_{1-6} haloalkoxy group, or a nitro group), a C_{1-6} alkoxycarbonyloxymethyl group, a phenylsulfonyl group optionally substituted with a (halogen atom, C_{1-6} alkyl group, C_{1-6} alkoxy group, a C_{1-6} haloalkyl group, a C_{1-6} haloalkoxy group, or a nitro group), an N-C_{1-6} alkyl-N-C_{1-6} alkylcarbonylaminomethyl group, or a N,N-di C_{1-6} alkylthiocarbamoylthiomethyl group;

X represents a hydrogen atom, a halogen atom, a nitro group, amino group, formyl group, or a C_{1-6} alkyl group;

Ar represents a 2-pyridyl group optionally substituted with (a hydrogen atom; a C_{1-6} alkyl group (optionally substituted with a halogen atom, C_{1-6} alkoxy group, hydroxy group, C_{1-6} alkylsulfonyl group, cyano group, hydroxyimino group, C_{1-6} alkoxyimino group, C_{1-6} alkylcarbonylhydrazino group, C_{1-6} alkoxycarbonyl group, or C_{1-4} alkoxy C_{1-4} alkoxy group); C_{2-6} alkenyl group (optionally substituted with a halogen atom, cyano group, C_{1-6}

alkoxycarbonyl group, or C_{1-4} alkoxy group); a C_{2-6} alkynyl group (optionally substituted with a halogen atom, a C_{1-4} alkoxy group, a hydroxy group, or a trimethylsilyl group); a mono C_{1-3} alkylamino group; a di C_{1-3} alkoxyamino group; an amino group; a C_{1-6} alkylthio group optionally substituted with a halogen atom; a C_{1-6} alkylsulfinyl group; a C_{1-6} alkylsulfonyl group; a C_{1-6} alkoxycarbonyl group; a C_{3-6} cycloalkyl group, C_{1-6} alkylcarbonyl group, cyanate group, thiocyanate group; a C_{1-6} alkoxy group optionally substituted with a halogen atom; a benzyloxy group; hydroxy group; a C_{1-6} alkylcarbonyloxy group, a C_{1-6} alkylcarbamoyloxy group, C_{1-6} haloalkylsulfonyloxy group; a 1-2-epoxy C_{2-6} alkyl group,
nitro group; a phenyl group (optionally substituted with a halogen atom, C_{1-6} alkyl group, C_{1-6} alkoxy group, or nitro group); or a benzyl group or cyano group (optionally substituted with a halogen atom, a C_{1-6} alkyl group, a C_{1-6} alkoxy group, or a nitro group)); a 2-pyrimidinyl group (optionally substituted with a halogen atom, C_{1-6} alkyl group, C_{1-6} alkoxy group, or C_{1-6} haloalkyl group); a 2-pyrazinyl group (optionally substituted with a halogen atom, C_{1-6} alkyl group, C_{1-6} alkoxy group, C_{1-6} haloalkyl group); or a 2-thiazolyl group (optionally substituted with a halogen atom, C_{1-6} alkyl group, C_{1-6} alkoxy group, C_{1-6} haloalkyl group.)